# Title: Methods of activation and specific applications of Carbon materials from natural sources

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**Ph. D. Seminar – II**
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# I. Introduction

## Activated Carbon Materials

- ➢ Highly porous structure
- ➢ High specific surface area and tunable porosity
- ➢ Hydrophobic and Hydrophilic surface coexist

Structure of Activated Carbon

## Applications

i. Catalysts

ii. Catalyst supports

iii. Energy storing media
(Methane, Hydrogen, Batteries, Electrodes for supercapacitors)

iv. Energy conversion (Fuel cells, Solar cells)

v. Effective in removing pollutants
(regulate $SO_x$ and $NO_x$ emissions from fuel combustion in automobiles)

**H. Fritzst Oeckli, Carbon 28 (1990) 6**
**Xiaoge Chen, S. Jeyaseelan, N. Graham, Waste Management 22 (2002) 755**

# Activated Carbon Materials – Challenges

- Production of activated carbon – Designing economic way
- **Major Sources**

  i. Coal based
  ii. Petroleum pitch based
  iii. Lignocellulosic materials

- **Exploration of new sources of carbon materials - Need of the hour**
- **Desired physico chemical properties**

  i. High specific surface area

  ii. Porosity

  iii. Surface functionality

  iv. Thermal stability

  v. Carbon content

  vi. Carbon purity and

  vii. Adsorptive capacity

Michal Kruk, Bruno Dufour, Ewa B. Celer, Tomasz Kowalewski, Mietek Jaroniec and Krzysztof Matyjaszewski,
J. Phys. Chem. B, 109 (2005) 9216
An-Hui Ru and Jing-Tang Zheng, Journal of Colloid and Interface Science, 236 (2001) 369
Junichi Hayashi, Atsuo Kazehaya, Katsuhiko Muroyama, A. Paul Watkinson, Carbon 28 (2000) 1873

# Activated Carbon Materials – Lignocellulosic Materials

- Thomas Alwa Edison has successfully employed carbon filament based on biomass in the invention of high-resistance incandescent lamp, where in either Pt or PtIr alloys have failed to provide an antidote

- **Lignocellulosic materials for Activated Carbon**

  i. Renewable

  ii. Inexhaustible supply

  iii. Evenly distribution around the globe

  iv. Viable option compared to fossil fuels

  V. Retention of the structural features of the original plant tissue (biotemplating feature)

  vi. High carbon content (because of easy removal of H and O)

**Approach - Rags to Riches**

**Challenge - Suitable production methods to be developed**

Great Leaders of the world, Stories of Achievement, Asa Don Dickinson, Garden City Publishing Co, Inc. Garden city, New York, 1937

Wenming Qiao, Yozo Korai, Isao Mochida, Yuuichi Hori, Takeshi Maeda, Carbon 40 (2002) 351

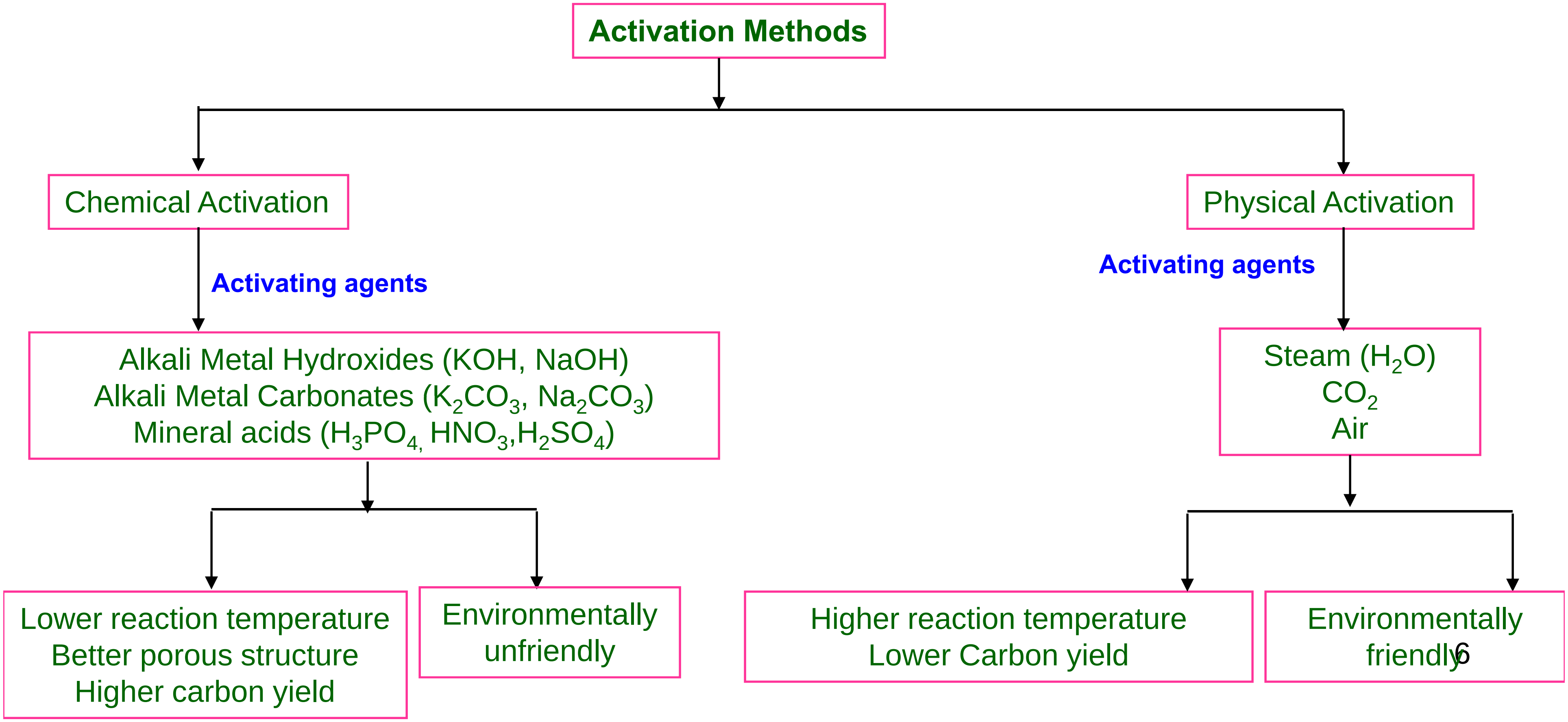
P. K. Malik, Journal of Hazardous Materials B113 (2004) 81

# Activated Carbon Materials – Methods of Activation

- Carbon is the only material where surface area values can be modulated from few $m^2/g$ to few 1000 $m^2/g$ due to the microarchitecture of the pores
- Variety of activating agents can be used
- Functional groups are easily introduced and altered

## Process of Activation

i. Creates porosity
ii. Generates desired surface functional groups



**Activation Methods**

Chemical Activation

**Activating agents**

Alkali Metal Hydroxides (KOH, NaOH)
Alkali Metal Carbonates ($K_2CO_3$, $Na_2CO_3$)
Mineral acids ($H_3PO_4$, $HNO_3$, $H_2SO_4$)

Lower reaction temperature
Better porous structure
Higher carbon yield

Environmentally unfriendly

Physical Activation

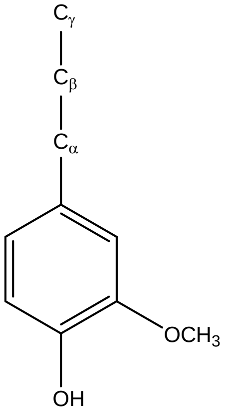
**Activating agents**

Steam ($H_2O$)
$CO_2$
Air

Higher reaction temperature
Lower Carbon yield

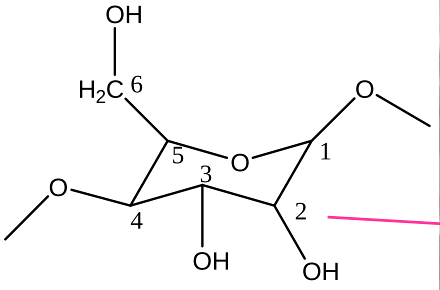
Environmentally friendly

# II. Activated Carbon from Calotropis Gigantea



Lignin

+



Cellulose

**Synthesis**
**i. Effect of Activating agents**
**Characterization**
**Application as Catalyst (HPW and W) support**

**Calotropis Gigantea - A waste land weed native of India**

# Activated Carbon from Calotropis Gigantea – Method of Preparation

Dry Stems

↓

Combustion in limited supply of air at 300 ºC in a muffle furnace

↓

Coal ground

↓

Sieved through 200 mesh

↓

Impregnation with Activating Agent

↓

Heat treatment, 800 ºC, 8 h, $N_2$ atm

↓

Treatment with HCl, carbon : acid = 1:10, wt./vol. 8h

↓

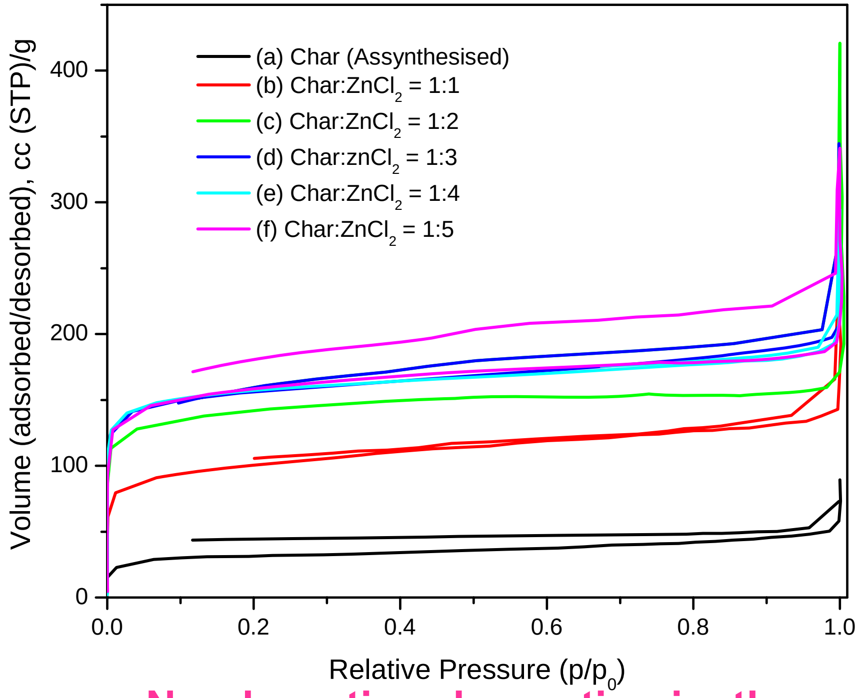
Filtered, washed with distilled water, Air dried and oven dried at 150 ºC

↓

Activated carbon

**B. Viswanathan, T. K. Varadarajan, P. Indra Neel, Patent No. IN 2007 CH00376**

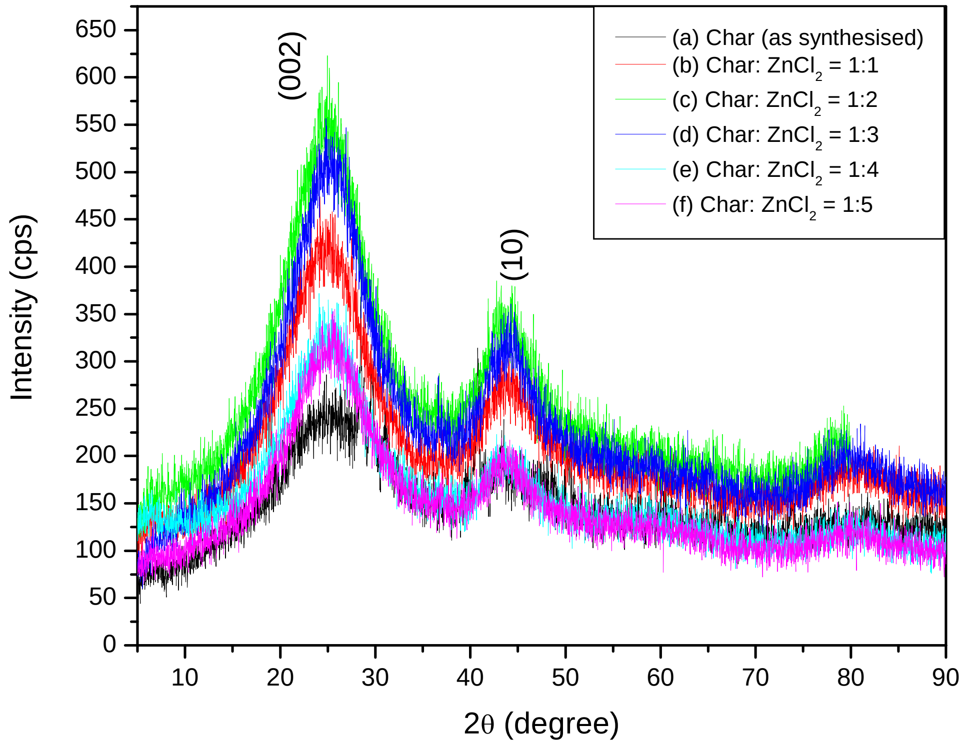
# Activated Carbon from Calotropis Gigantea - Textural Properties



$N_2$ adsorption-desorption isotherms of (a) as synthesized (char), activated carbon with a Char to $ZnCl_2$ ratio (wt./wt.%) of (b) 1:1, (c) 1:2, (d) 1:3, (e) 1:4 and (f) 1:5

| S. No. | Sample | $ZnCl_2$ : C (wt./wt.%) | $S_{BET}$ ($m^2/g$) | $V_P$ ($cm^3/g$) | Mean Pore Diameter[ii] (nm) |
|---|---|---|---|---|---|
| 1 | Char | 0 | 97 | 0.08 | 3.3 |
| 2 | AC1 | 1 | 356 | 0.21 | 2.36 |
| 3 | AC2 | 2 | 493 | 0.25 | 2.03 |
| 4 | AC3 | 3 | 564 | 0.30 | 2.13 |
| 5 | AC4 | 4 | 573 | 0.29 | 2.02 |
| 6 | AC5 | 5 | 553 | 0.29 | 2.1 |

# Activated Carbon from Calotropis Gigantea - Structural Properties



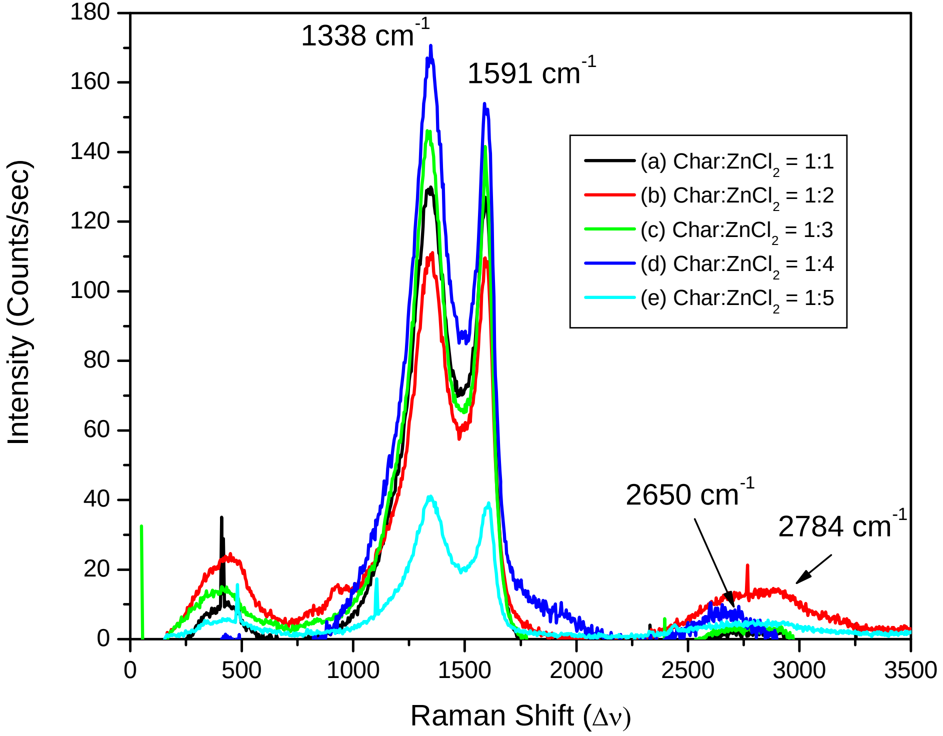
XRD pattern of (a) as synthesized (char), activated carbon with a Char to $ZnCl_2$ ratio (wt./wt.%) of (b) 1:1, (c) 1:2, (d) 1:3, (e) 1:4 and (f) 1:5

- ➢ Interlayer spacing values, $d_{002}$, almost remained unchanged with impregnation ratio of $ZnCl_2$ to char
- ➢ $d_{002}$ values of AC's were greater than the $d_{002}$ value of pure graphitic carbon structure (0.335 nm)
- ➢ $L_C$ values of AC's are of the order of 1 nm
- ➢ $L_c$ values decreased with an increase in the amount of the activating agent
- ➢ c and a values are 0.06708 nm and 0.2461 nm respectively for typical graphitic carbon structure
- ➢ The AC's contained roughly about 2 cell length along the c-direction and about 14 – 16 cell lengths along the a - direction

| S. No. | Sample | $ZnCl_2$ : C (wt./wt.%) | $d_{002}$ (nm) | $L_c$ (nm) | $L_a$ (nm) |
|---|---|---|---|---|---|
| 1 | iAC1 | 1 | 0.356 | 1.04 | 3.94 |
| 2 | AC2 | 2 | 0.356 | 1.02 | 3.50 |
| 3 | AC3 | 3 | 0.353 | 1.03 | 3.96 |
| **4** | **AC4** | **4** | **0.356** | **0.91** | **3.72** |
| 5 | AC5 | 5 | 0.350 | 0.94 | 3.80 |

**i. AC**

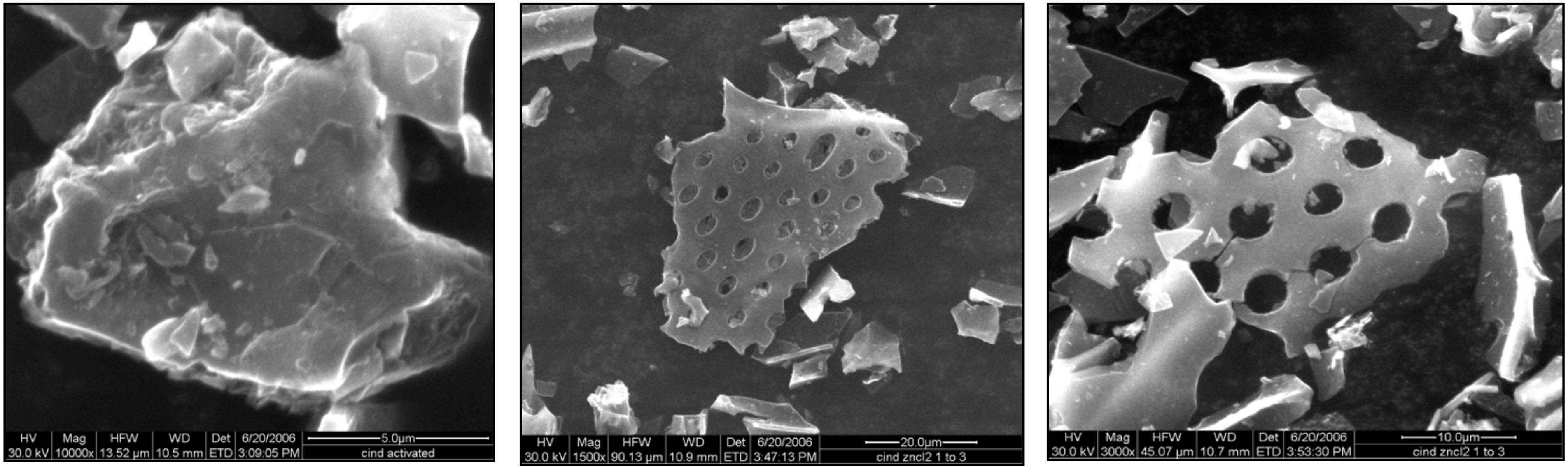
# Activated Carbon from Calotropis Gigantea - Structural Properties



Confocal Raman spectra of activated carbon materials with a Char to ZnCl$_2$ ratio (wt./wt.%) of (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4 and (e) 1:5

| S. No. | Sample | ZnCl$_2$ : C (wt./wt.%) | Peak Intensity Frequency, $\nu_{x}$, cm$^{-1}$ | | R = $I_D/I_G$ | $L_a$ (nm) = 4.4/R (From Raman) | $L_a$ (nm) (from XRD) |
|---|---|---|---|---|---|---|---|
| | | | G band | D band | | | |
| 1 | $^{i}$AC1 | 1 | 1591 | 1348 | 1.40 | 3.14 | 3.94 |
| 2 | AC2 | 2 | 1591 | 1355 | 1.42 | 3.09 | 3.50 |
| 3 | AC3 | 3 | 1591 | 1331 | 1.33 | 3.30 | 3.96 |
| **4** | **AC4** | **4** | **1587** | **1348** | **1.48** | **2.97** | **3.72** |
| 5 | AC5 | 5 | 1606 | 1348 | 1.53 | 2.87 | 3.80 |

# Activated Carbon from Calotropis Gigantea - Morphology



(a) (b) (c)

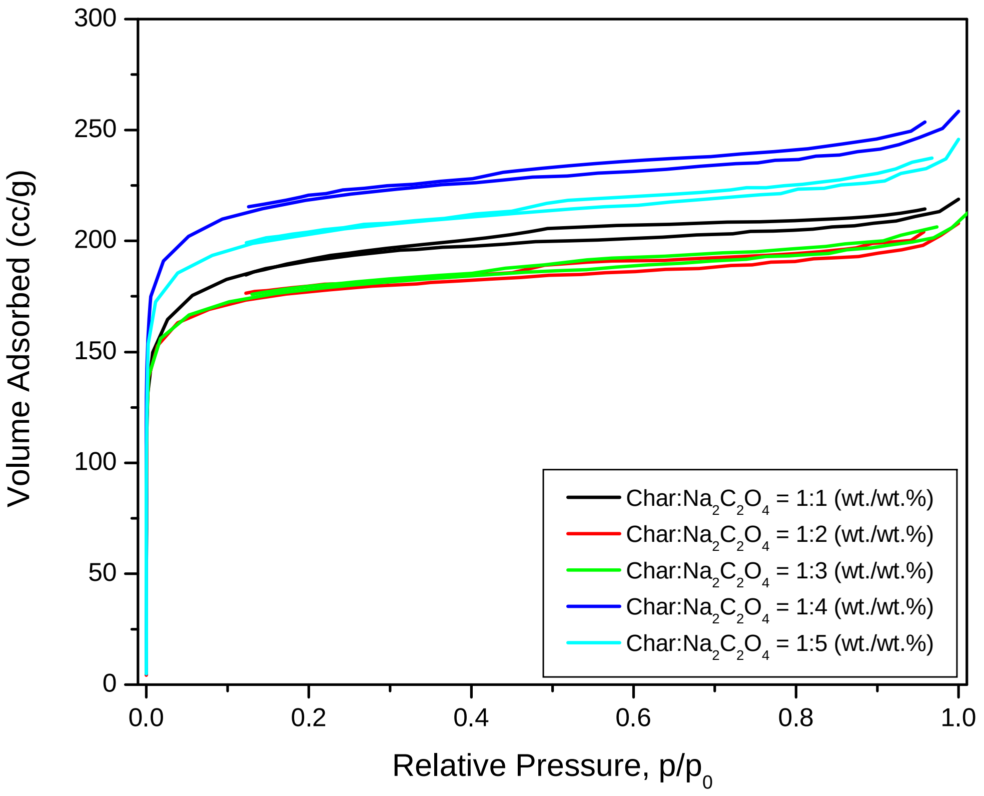
SEM images of Activated Carbon from Calotropis Gigantia (a) thermal activation alone (at 800 °C, 8 h, in $N_2$ atm.)(b) activated with $ZnCl_2$ (wt/wt. % ratio of Char:$ZnCl_2$ is 1:3) at 1500 x and (c) at 3000 x

- ➢ Carbon sample activated by thermal means alone is Nonporous and Heterogeneous with steps and kinks seen on the surface

- ➢ Activation with $ZnCl_2$ transformed a non porous carbon samples in to Porous carbon with well aligned uniform cylindrical pores of diameter (size) 2.4 µm

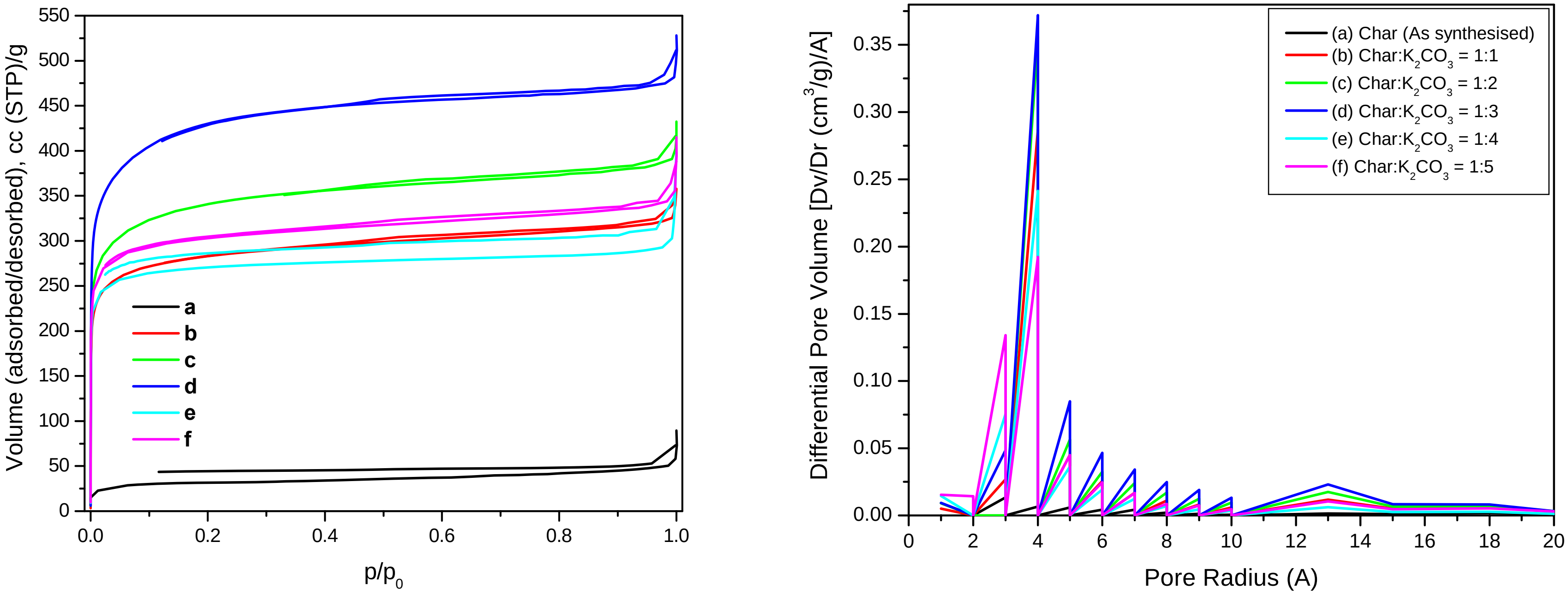
- ➢ Activating agent is inevitable for the creation of porous carbon structure

# Activated Carbon from Calotropis Gigantea – $Na_2C_2O_4$ as activating agent



| **S. No.** | **Carbon Material** | **$Na_2C_2O_4$ : Char (wt./wt.%)** | **$S_{BET}$ ($m^2/g$)** | **$V_P$ ($cm^3/g$)** |
|---|---|---|---|---|
| 1 | Char | 0 | 97 | 0.08 |
| 2 | AC1 | 1 | 707 | 0.33 |
| 3 | AC2 | 2 | 647 | 0.31 |
| 4 | AC3 | 3 | 655 | 0.32 |
| **5** | **AC4** | **4** | **785** | **0.39** |
| 6 | AC5 | 5 | 735 | 0.37 |

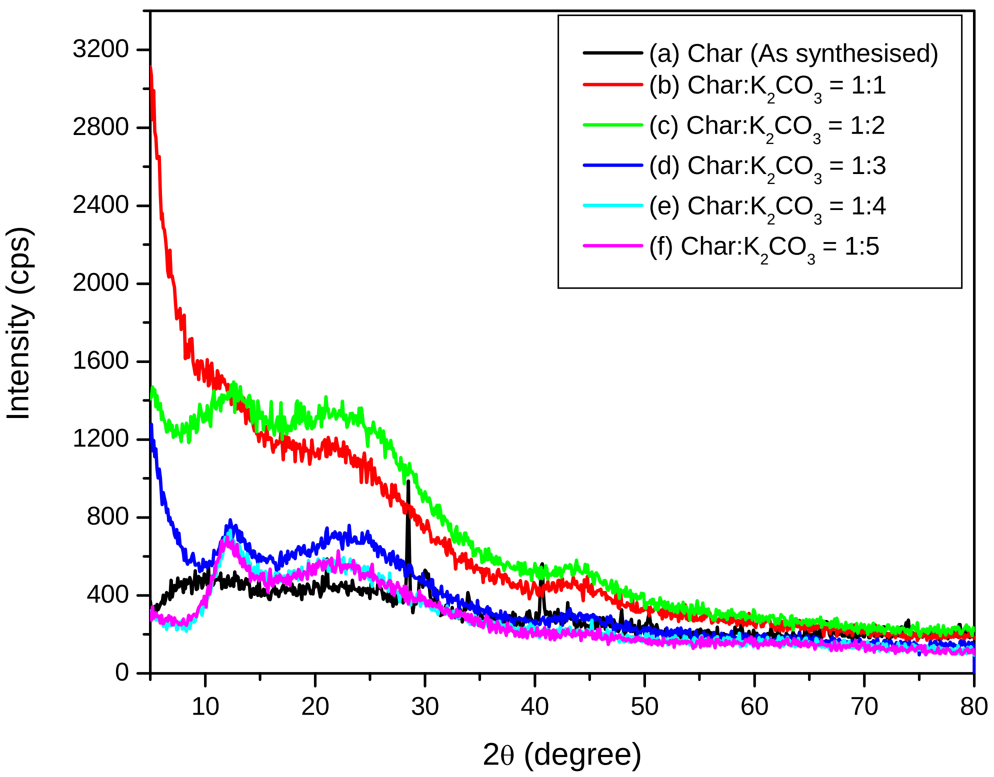
# Activated Carbon from Calotropis Gigantea - Textural Properties



$N_2$ adsorption-desorption isotherms and PSD curves of carbon materials
(a) as synthesized (char), activated carbon with a char to $K_2CO_3$ ratio (wt./wt.%) of
(b) (b) 1:1, (c) 1:2, (d) 1:3, (e) 1:4 and (f) 1:5

| **S. No.** | **Sample** | **$K_2CO_3$ : C (wt./wt.%)** | **$S_{BET}$ ($m^2$/g)** | **$V_P$ ($cm^3$/g)** | **Mean Pore Diameter$^{ii}$ (nm)** |
|---|---|---|---|---|---|
| 1 | Char | 0 | 97 | 0.08 | 3.3 |
| 2 | $^{i}$AC1 | 1 | 892 | 0.50 | 2.2 |
| 3 | AC2 | 2 | 1083 | 0.59 | 2.1 |
| 4 | AC3 | 3 | 1296 | 0.73 | 2.2 |
| 5 | AC4 | 4 | 765 | 0.45 | 2.3 |
| 6 | AC5 | 5 | 922 | 0.53 | 2.3 |

# Activated Carbon from Calotropis Gigantea - Structural Properties



**i. Two broad diffraction peaks centered at 2θ values of 10 and 22° observed**

**ii. The broad diffraction peak at a 2θ value of 22° is characteristic of the presence of lignin component**

**iii. Inherent plant micro structure is retained Upon activation with $K_2CO_3$ in inert atmosphere (biotemplating feature)**

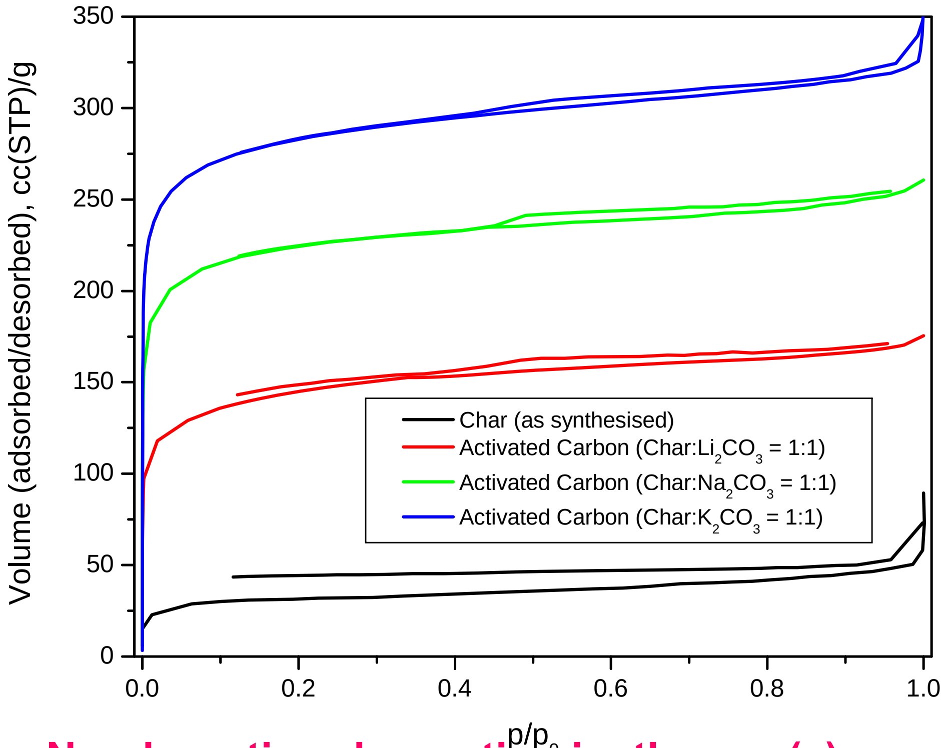
**iv. Silica and mineral content removed by Treatment with NaOH and HCl**

**v. New diffraction peak originated at a 2θ value of 43.5 originated upon activation**

**vi. The diffraction peak at the 2θ value of 43.5° is attributed to reflection from (10) plane characteristicof turbostratic carbon containing small hexagonal layer units of carbon**

**XRD pattern of carbon materials prepared from Calotropis Gigantea,**
**(a) as synthesized (char), activated carbon with a Char to K2CO3 ratio (wt./wt.%) of**
**(b) (b) 1:1, (c) 1:2, (d) 1:3, (e) 1:4 and (f) 1:5**

# Textural properties of Carbon Materials from Calotropis Gigantea
# Effect of the nature of *Cation* of the Alkali Metal Carbonate



**i. The specific surface area of the activated carbon is dependent on the radii of the cation of the activating agent empolyed**

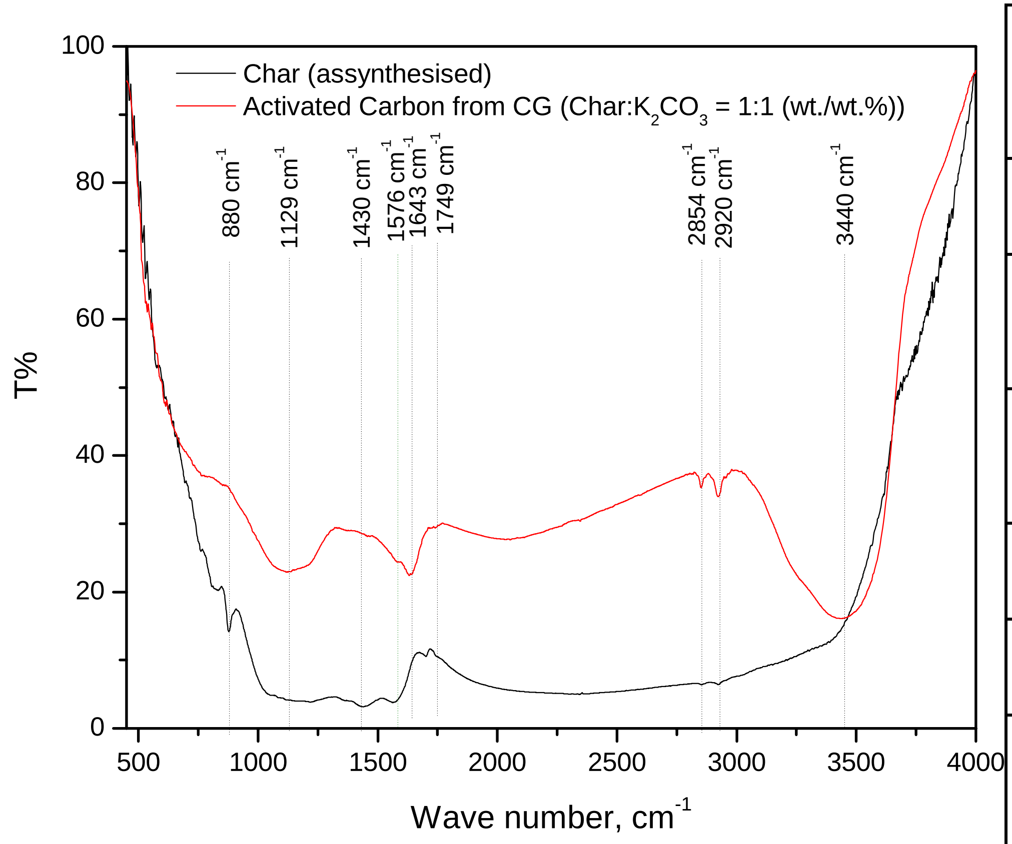
$N_2$ adsorption-desorption isotherms (a) as synthesized (char) and activated carbon with a char to activating agent ratio (wt./wt.%) of 1:1, (b) $Li_2CO_3$ activation (c) $Na_2CO_3$ activation and (d) $K_2CO_3$

| S. No. | Activating agent | Ionic radii of the cation (Å) | $E^0$ (V)$^{a, b}$ | Textural properties of Carbon Materials | |
|---|---|---|---|---|---|
| | | | | Specific Surface Area ($m^2$/g) | Specific Pore Volume (cc/g) |
| 1 | $Li_2CO_3$ | 0.60 | -3.0 | 480 | 0.263 |
| 2 | $Na_2CO_3$ | 0.96 | -2.7 | 811 | 0.395 |
| **3** | **$K_2CO_3$** | **1.33** | **-2.9** | **892** | **0.497** |

a. $M+ (aq) + e \rightleftharpoons M (s)$

b. The standard redox potential of activated carbon is + 0.24 V

# Carbon Materials from Calotropis Gigantea – Surface Functionality

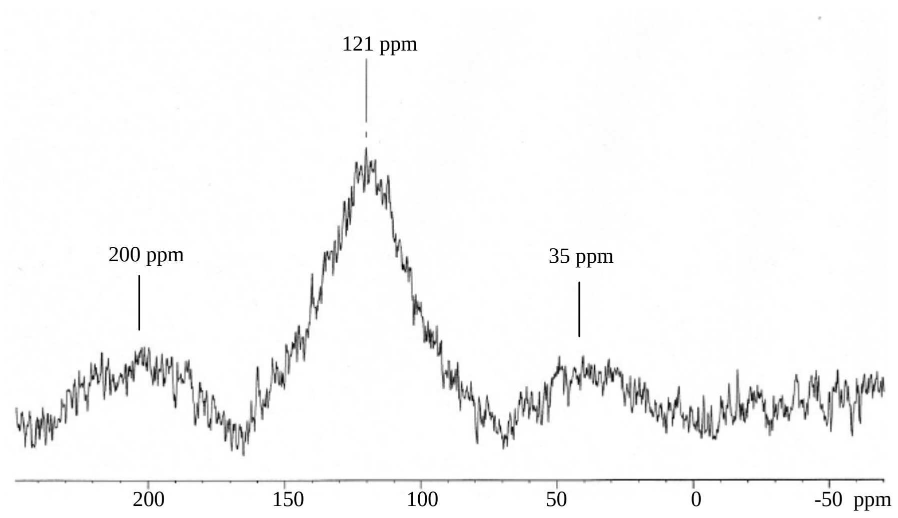


**FT – IR spectra of Char (as synthesised) and Activated Carbon (Char:$K_2CO_3$ = 1:1, wt./wt.%)**

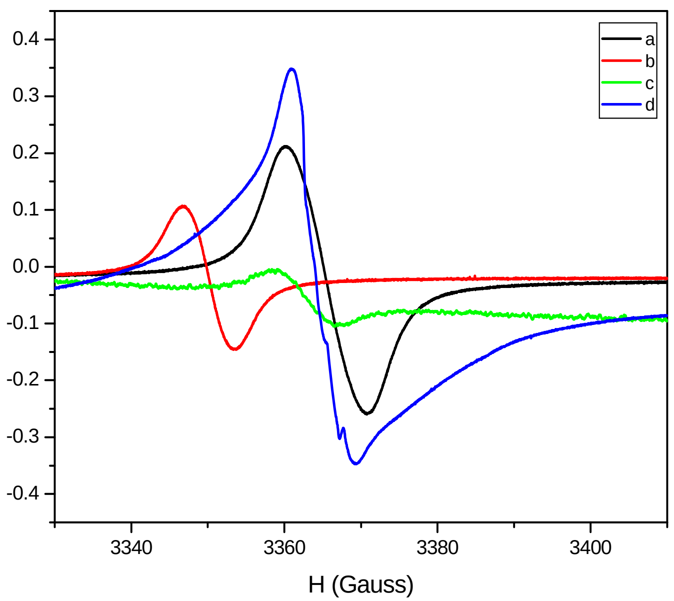
- **Activation with $K_2CO_3$ generated C=O (carbonyl and carboxylic) groups on the carbon surface**

| Band position, ν, $cm^{-1}$ | Assignment | |
|---|---|---|
| | Char | Activated Carbon |
| 3440 | O-H stretching of adsorbed $H_2O$ | O-H stretchingof adsorbed $H_2O$ |
| 2920 | Asymmetric C-H stretching vibration of methylene group | Asymmetric C-H stretching vibration of methylene group |
| 2845 | Symmetric C-H stretching vibration of methylene group | Symmetric C-H stretching vibration of methylene group |
| 1749 | - | C=O stretching vibration of carboxylic group |
| 1643 | - | C=O (carbonyl) stretching in quinone |
| 1576 | C=C stretching vibration of aromatic ring | C=C stretching vibration of aromatic ring |
| 1430 | In plane bending vibration of C-H in methylene group | In plane bending vibration of C-H in methylene group |
| 1129 | - | C-O stretching in carboxylic group |
| 880 | Out of plane deformation vibration of C-H groups in aromatic structure | - |

# Carbon Materials from Calotropis Gigantea – $^{13}$C MAS NMR and EPR studies



$^{13}$C MAS NMR spectrum of the Char



EPR spectra of (a) char (b) char treated with NaOH followed by HCl, (c) char activated with $K_2CO_3$ (char:$K_2CO_3$ (wt./wt.%) =1:3) and (d) DPPH

- Strong resonance line near 121 ppm - carbon nuclei in the aromatic planes
- Broad resonance signal at 35 ppm - aliphatic chains of polymethylene type
- Broad resonance signal at 200 ppm attributable to ketonic carbon groups

| S. No. | Carbon Material | g-factor value | ΔH (in Gauss) Peak to peak separation | Spin Concentration per gram of carbon material |
|---|---|---|---|---|
| 1 | Char (as synthesized) | 2.00092 | 11.0 | 0.73 x $10^{19}$ |
| 2 | Char (base and acid treated) | 1.99980 | 6.0 | 0.33 x $10^{19}$ |
| 3 | Char activated with $K_2CO_3$ (char:$K_2CO_3$ = 1:3, wt./wt.%) | 2.00058 | 9.5 | 0.15 x $10^{16}$18 |

## Activated Carbon from Calotropis Gigantea – Necessity of Activating Agent

| Carbon Material | $S_{BET}$ ($m^2/g$) | $V_P$ (cc/g) | Density (g/cc) |
|---|---|---|---|
| Char (As synthesized) | 97 | 0.08 | 0.31 |
| Base and Acid treated sample | 202 | 0.12 | 0.36 |
| Thermal activated sample (800 °C, 8 h, $N_2$ atm) | 381 | 0.12 | 0.37 |

- **No significant improvement in $S_{BET}$ with out activating agent**

## Activated Carbon from Calotropis Gigantea – Optimization of Activation Time

| Duration of Activation ( h) | $S_{BET}$ ($m^2/g$) | $V_P$ (cc/g) | Density (g/cc) |
|---|---|---|---|
| **2** | **1236** | **0.59** | **0.28** |
| 4 | 1161 | 0.54 | 0.28 |
| 6 | 1086 | 0.52 | 0.28 |
| **8** | **1296** | **0.73** | **0.28** |

- **The optimum period of activation only is 2 h**

## Activated Carbon from Calotropis Gigantea – Comparison with Commercial Activated Carbon Samples

| Carbon Material | $S_{BET}$ ($m^2/g$) | $V_P$ (cc/g) | Density (g/cc) |
|---|---|---|---|
| **CDX 975** | **215** | **0.28** | **0.23** |
| **Vulcan XC 72 R** | **224** | **0.46** | **0.33** |
| **Black Pearl 2000** | **1012** | **1.15** | **0.15** |
| **Nuchar** | **1271** | **0.33** | **1.05** |
| **Activated Carbon from Calotropis Gigantea** | **1291** | **0.73** | **0.28** |

- **Activated Carbon produced from Calotropis Gigantea showed higher $S_{BET}$ and $V_p$ than commercial activated carbon materials**

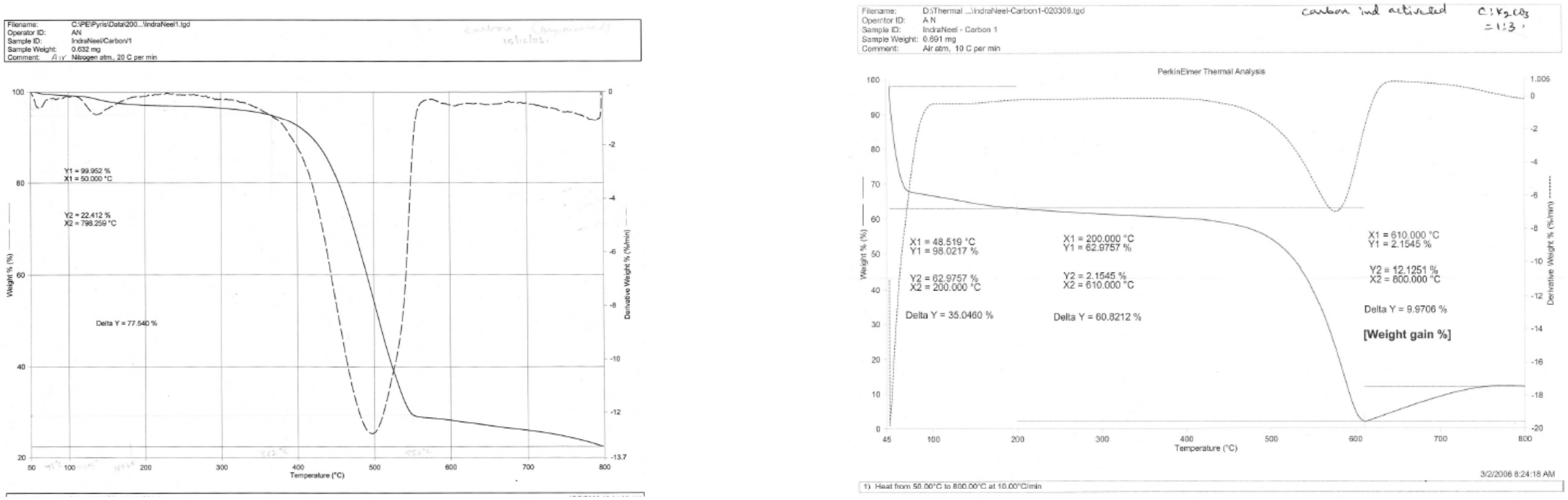
# Activated Carbon from Calotropis Gigantea – Different Activating Agents

| S. No. | Activating agent | $S_{BET}$ ($m^2/g$) | $V_p$ $cm^3/g$ | Type of isotherm/porosity |
|---|---|---|---|---|
| 1 | $Li_2CO_3$ | 478 | 0.26 | Type I (Microporous) |
| 2 | $Na_2CO_3$ | 811 | 0.40 | Type I (Microporous) |
| **3** | **$K_2CO_3$** | **892** | **0.50** | **Type I (Microporous)** |
| 4 | $Ca(CO_3)_2$ | 524 | 0.33 | Type I (Microporous) |
| 5 | $Ba(CO_3)_2$ | 170 | 0.10 | Type I (Microporous) |
| 6 | $Zn(CO_3)_2$ | 626 | 0.30 | Type I (Microporous) |
| 7 | NaCl | 400 | 0.20 | Type I (Microporous) |
| 8 | NaBr | 319 | 0.16 | Type I (Microporous) |
| 9 | KBr | 275 | 0.10 | Type I (Microporous) |
| 10 | NaI | 58 | 0.04 | Type I (Microporous) |
| 11 | CaO | 521 | 0.25 | Type I (Microporous) |
| 12 | $Ca(OH)_2$ | 189 | 0.11 | Type I (Microporous) |
| 13 | $CaCl_2$ | 156 | 0.09 | Type I (Microporous) |
| 14 | $Ba(OH)_2$ | 152 | 0.08 | Type I (Microporous) |
| 15 | $Al_2O_3$ | 174 | 0.17 | Type IV (Mesoporous) |
| 16 | $Al(NO)_3$ | 253 | 0.19 | Type I (Microporous) |
| 17 | Urea | 439 | 0.21 | Type I (Microporous) |
| 18 | Sodium acetate | 548 | 0.26 | Type I (Microporous) |
| 19 | Sodium oxalate | 707 | 0.33 | Type I (Microporous) |
| 20 | Sodium potassium tartarate | 394 | 0.20 | Type I (Microporous) |
| 21 | Sodium citrate | 419 | 0.20 | Type I (Microporous) |
| 22 | Sodium tartarate | 394 | 0.20 | Type I (Microporous) |
| 23 | Citric acid | 127 | 0.07 | Type I (Microporous) |
| 24 | Tartaric acid | 42 | 0.04 | Type I (Microporous) |
| 25 | Oxalic acid | 317 | 0.14 | Type I (Microporous) |

# Carbon Materials from Calotropis Gigantea – Chemical composition

| Element (wt. %) | Carbon Materials from Calogropis Gigantea | | |
|---|---|---|---|
| | Char (As synthesized) | Base and Acid treated (NaOH and HCl) treated | Activated with $K_2CO_3$ ($Char:K_2CO_3 = 1:3$) |
| **Carbon** | 73.13 | 77.62 | 80.04 |
| **Hydrogen** | 2.61 | 2.63 | 3.50 |
| **Nitrogen** | 0.81 | 0.82 | 0.67 |
| **Sulphur** | 0.36 | 0.33 | 0.36 |
| **Total** | 76.91 | 81.40 | 84.57 |
| **Ash content** | 12.7 | 4.0 | 1.8 |
| **Oxygen*** | 10.39 | 14.6 | 13.63 |

# Carbon Materials from Calotropis Gigantea – Thermal Stability


Filename: C:\PE\Pyris\Data\200...\IndraNeel1.tgd
Operator ID: AN
Sample ID: IndraNeel/Carbon/1
Sample Weight: 0.632 mg
Comment: Air Nitrogen atm., 20 C per min

Filename: D:\Thermal ...\IndraNeel-Carbon1-020308.tgd
Operator ID: A N
Sample ID: IndraNeel - Carbon 1
Sample Weight: 0.691 mg
Comment: Air atm, 10 C per min

carbon ind activated C:K2CO3 =1:3

1) Heat from 50.00°C to 800.00°C at 10.00°C/min

3/2/2008 8:24:18 AM

TG-DTG curves for (a) Char and (b) activated carbon from Calotropis Gigantea in air at a heating rate of 20 ºC/min

- ➢ **Thermal stability improved upon activation with $K_2CO_3$**

# Heteropoly acids – Unique features

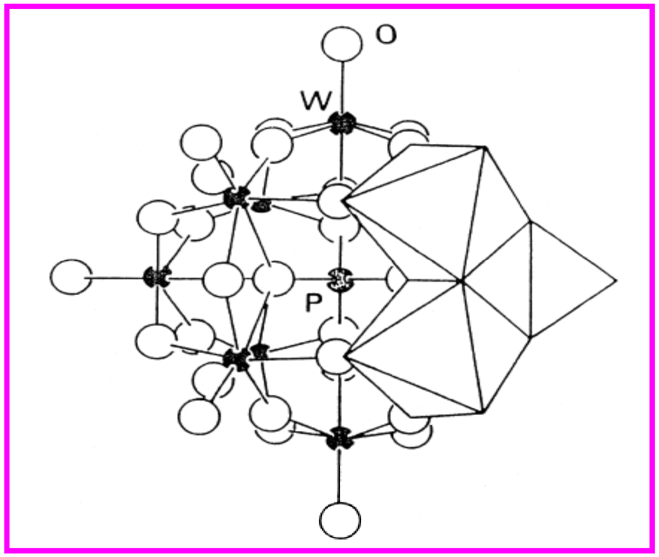
- Multifunctional
- Structural mobility
- Strong Bronsted acidity
- Homogeneous as well as heterogeneous
- Efficient oxidants
- Easy alteration of chemical composition
- Structure preserved upon substitution
- High solubility in polar solvents
- Environmentally friendly

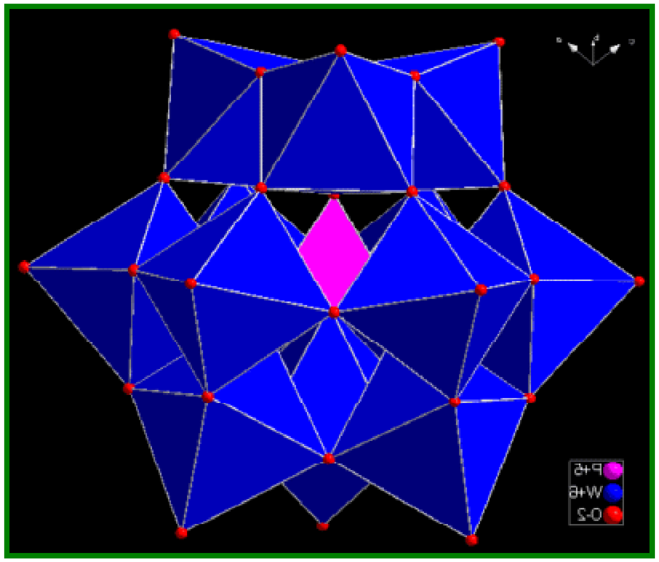
## Draw backs :

- Low specific surface area (1-10 $m^2/g$)
- Thermally stable only up to 773 K

## Solution :

- ✓ Search for suitable carrier





Keggin ion structure

# Activated Carbon from Calotropis Gigantea (ACCG) – Support for $H_3PW_{12}O_{40}$ (HPW)

**Catalyst Preparation:** Dry impregnation

0.2 g HPW in distilled water

↓

1.8 g Activated Carbon in distilled water

↓ Stirring at RT for 6 h

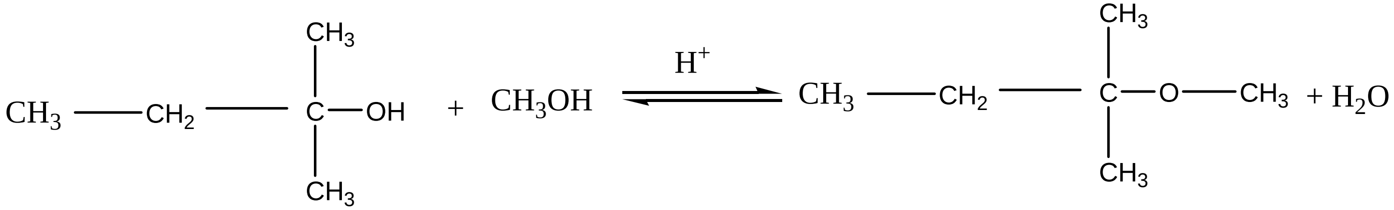
Impregnation of C with HPW

↓ Drying at 80 °C in water bath

10 wt.% HPW/ACCG, Black Pearl, Vulcan XC 72 R, CDX 975

**Evaluation of Catalytic Activity of HPW/C catalysts:**

**Reaction:** Vapour phase synthesis of tert – amyl methyl ether (TAME) from tert – amyl alcohol and MeOH



$$CH_3CH_2C(CH_3)_2OH + CH_3OH \overset{H^+}{\rightleftharpoons} CH_3CH_2C(CH_3)_2OCH_3 + H_2O$$

- Conventional gasoline – 0 to 3.7 % oxygen content
- Incomplete fuel combustion
- Emission of noxious gases
- Oxygenates facilitates efficient combustion
- Fuel oxygenate (Octane enhancer)
- Replacment for Tetraethyl lead (TEL)

**TAME** – Useful gasoline additive
Improve burning characteristics of Fuels
Reduces CO emissions in automobiles
High Octane No. 106
Low volatility

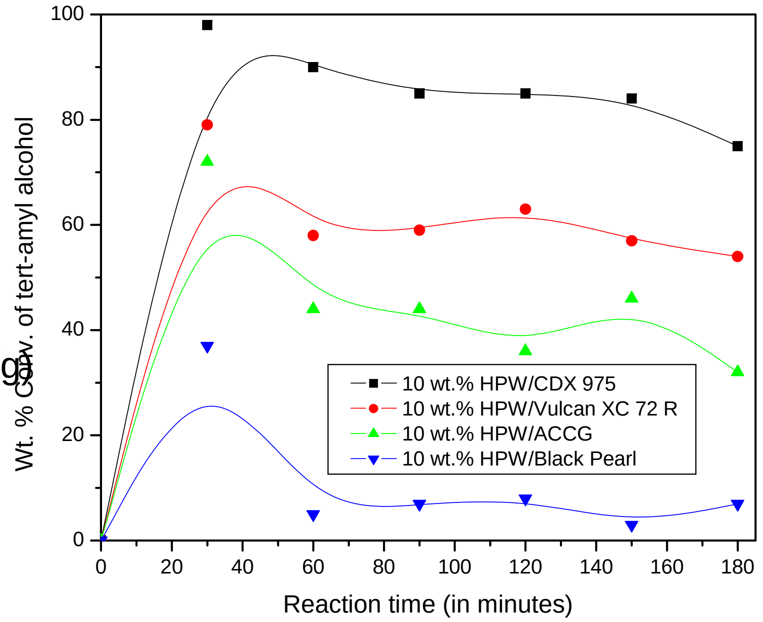
# HPW/C for the Synthesis of TAME (t-amyl methyl ether)

| **Catalyst** | **10 wt% HPW/CDX 975** | | | **10 wt% HPW/Vulcan XC72R** | | | **10 wt% HPW/Carbon from Calotropis Gigantea** | | | **10 wt% HPW/Black pearl** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Reaction Time in min** | **Wt% conv. of TAA** | **% selectivity** | | **Wt% conv. of TAA** | **% selectivity** | | **Wt% conv. of TAA** | **% selectivity** | | **Wt% conv. of TAA** | **% selectivity** | |
| | | **TAME** | **olefins** | | **TAME** | **olefins** | | **TAME** | **olefins** | | **TAME** | **olefins** |
| 30 | 98 | 60 | 40 | 79 | 84 | 16 | 72 | 52 | 48 | 37 | 45 | 55 |
| 60 | 90 | 50 | 40 | 58 | 94 | 6 | 44 | 57 | 43 | 5 | 19 | 81 |
| 90 | 85 | 51 | 49 | 59 | 86 | 15 | 44 | 47 | 53 | 7 | 41 | 59 |
| 120 | 85 | 60 | 40 | 63 | 75 | 25 | 36 | 64 | 36 | 8 | 61 | 39 |
| 150 | 84 | 41 | 59 | 57 | 95 | 5 | 46 | 60 | 40 | 3 | 44 | 56 |
| 180 | 75 | 65 | 35 | 54 | 87 | 13 | 32 | 73 | 37 | 7 | 47 | 53 |

Reaction temperature = 100 ºC
Mole ratio of the feed, MeOH : TAA = 10:1
Flow rate of the feed = 10 ml/h
Flow rate of carrier gas ($N_2$) = 30 ml/min
GC Column used = OV 101 Packed column

## Activity Order:

- HPW/CDX 975 (215 $m^2/g$) > HPW/Vulcan XC 72 R (224 $m^2/g$) > HPW/ACCG (1012 $m^2/g$)) > HPW/Black Pearl (1091 $m^2/g$))
- High activity of the catalyst is derived from the support (CDX 975) with the least specific surface area
- CDX 975 support offers optimum dispersion and thereby resulting in mild acidity needed for etherification reaction because of the relatively low specific surface area value



Plot of wt. % conversion of amyl$^t$ alcohol Vs reaction time (in min)

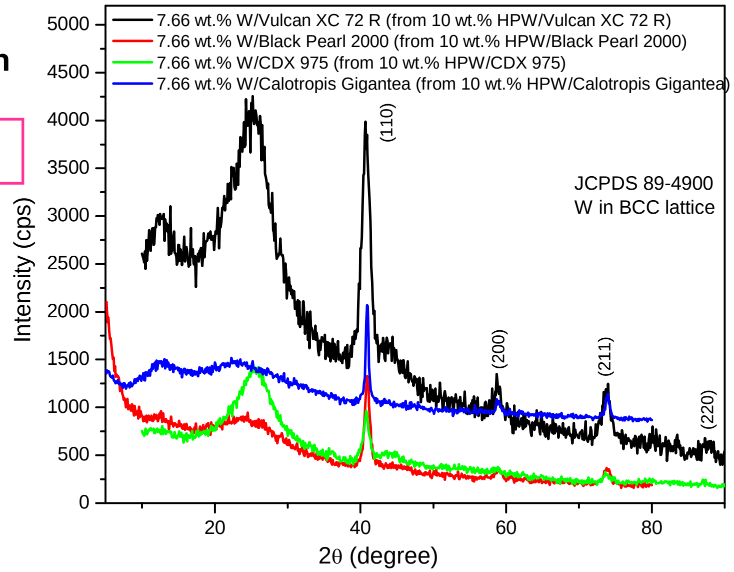
# Activated Carbon from Calotropis Gigantea (ACCG) – Support for W

## Catalyst Preparation: Dry impregnation followed by $H_2$ reduction

**10 wt.% HPW/ACCG, Black Pearl, Vulcan XC 72 R, CDX 975**

↓ **Reduction in $H_2$ atm. at 800 °C for 8 h**

**7.66 wt. % W/ACCG, Black Pearl, Vulcan XC 72 R, CDX 975**



## Hydrogenation reaction - Significance

- ❖ Prime and foremost reaction in HDS and HDN reactions
- ❖ Around 80 % of the HDS of 4, 6 – DMDBT proceeds via the hydrogenation route where in the adsorbed 4, 6 – DMDBT is first hydrogenated and then the hydrogenated compound is desulphurized
- ❖ Hydrogenation of olefins – An important reaction in chemical industry
- ❖ Relevant to petrochemical industries
- ❖ Many catalytic processess and applications in the pharmaceutical, agrochemical and petrochemical industries is based on catalytic hydrogenation of unsaturated hydrocarbons by heterogeneous catalysts

➢ **Hydrogenation activity of W/C catalysts is evaluated by the vapour phase hydrogenation of Cyclohexene**

## Summary:

1. Calatropis Gigantea is an appropriate precursor for activated carbon with desirable properties

2. Among several activating agents, $K_2CO_3$ showed best performance

3. In addition to the creation of porosity, $K_2CO_3$ activation oxidized the carbon surface generating C=O (carbonyl and carboxylic groups)

4. The optimum conditions for the activation with $K_2CO_3$ are : Char:Activating agent (wt./wt.% ratio) = 1:3, Activation temperature = 800 °C, Activation time = 2 h, Carbon:HCl (wt.% /vol.% = 1:10)

5. All the activating agents tested induced microporosity except $Al_2O_3$ which resulted in the formation of mesopores (mean pore diamter = 3.9 nm)

6. Impurities in the carbon precursor (silica and alkali and alkaline earth metals) were reduced from 12.7 wt.% in the char to 1.8 wt.% in the activated carbon with the method of activation employed

7 The presence of paramagnetic centers (dangling bonds) reduced upon activation. EPR spectroscopic studies indicated the level of impurites in the original char and the activated carbon

8. The activated carbon from Calotropis Gigantea is employed as support for HPW for the vapour phase synthesis of TAME. HPW/ACCG showed higher catalytic activity than HPW/Black Pearl and comparable performance with HPW/Vulcan XC 72 R

9. The activated carbon from Calotropis Gigantea is employed as support for W for the vapour phase hydrogenation of cyclohexene. HPW/ACCG showed comparable catalytic activity with that of W/Vulcan XC 72 R and W/CDX 975

# III. Activated Carbon from Limonea Acidissima

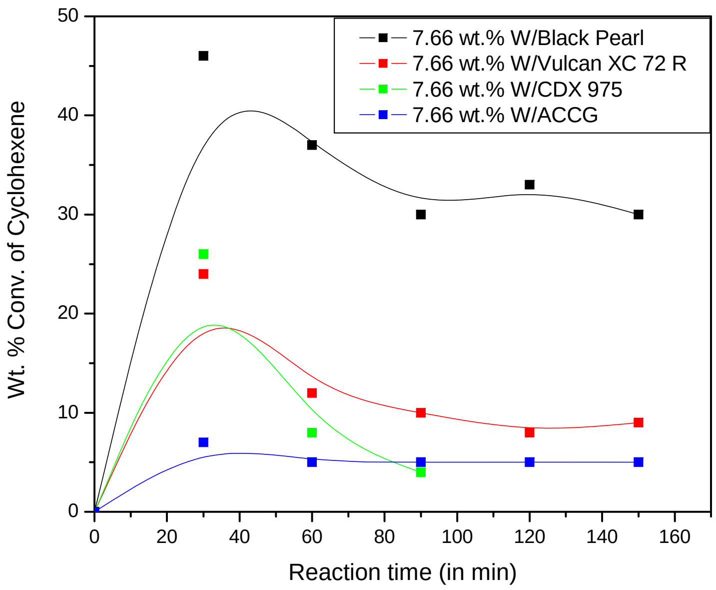
**Source of carbon : Shell of wood apple**
**Tree : wood apple tree, Bilva patra, Bel, Elephant wood**
**Binomial nomenclature: Feronia Limonia, Limonia Acidissima, Limonia elaphantum**
**Habitat : Found all over the deciduous forests in India**

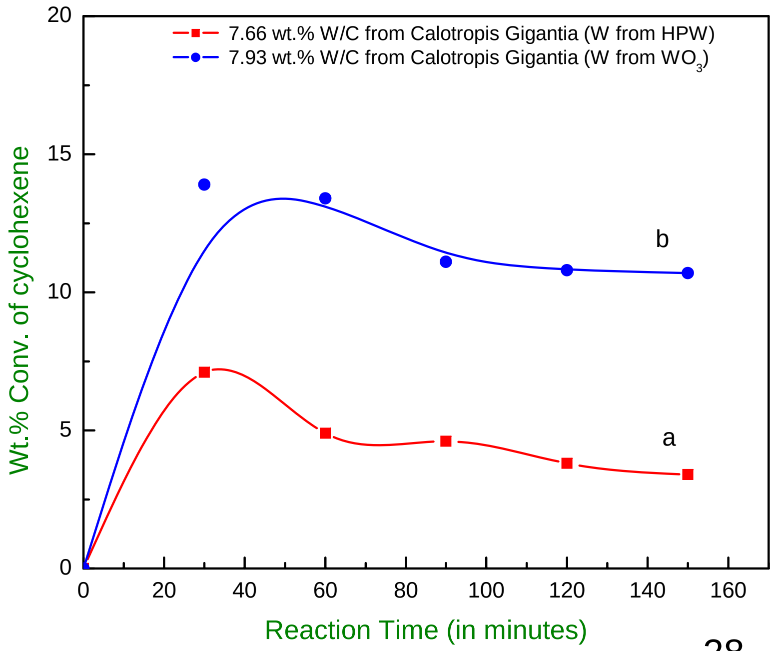
Synthesis
Characterization
Application as Catalyst (Pt) Support

**Dry Shells**
**Soaking in KOH solution (50 wt.%), 12 h**
**KOH impregnated Shells**
**Tubular furnace, 800 °C, 2 h, $N_2$ atm.**
**Carbonization & Activation**
**Carbon Product**
**Treatment with $HNO_3$, carbon : acid = 1:15, wt./wt. % 8h**
**Refluxing for 3 h, 60 °C**
**Filtered, washed with distilled water, Air dried and oven dried at 150 ºC**
**Activated carbon**

# Activated Carbon from Calotropis Gigantea (ACCG) – Support for W

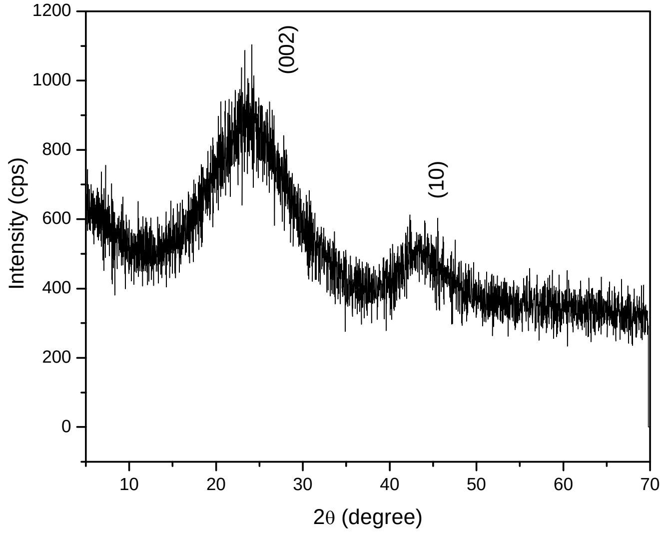
| **Catalyst** | **W/Black Pearl** | | | **W/Vulcan XC 72 R** | | | **W/CDX 975** | | | **W/ACCG** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Reaction Time in min** | **Wt% conv. of Cyclo hexene** | **% selectivity** | | **Wt% conv. of Cyclo hexene** | **% selectivity** | | **Wt% conv. of Cyclo hexene** | **% selectivity** | | **Wt% conv. of Cyclo hexene** | **% selectivity** | |
| | | **Cycloh exane** | **Other product** | | **Cyclo hexane** | **Other product** | | **Cyclo hexane** | **Other product** | | **Cyclo hexane** | **Benzene** |
| 30 | 46 | 76 | 24 | 24 | 84 | 16 | 26 | 79 | 11 | 7 | 51 | 49 |
| 60 | 37 | 85 | 15 | 12 | 82 | 18 | 8 | 88 | 12 | 5 | 39 | 61 |
| 90 | 30 | 85 | 15 | 10 | 83 | 17 | 4 | 87 | 13 | 5 | 44 | 56 |
| 120 | 33 | 86 | 14 | 8 | 82 | 18 | | | | 5 | 36 | 64 |
| 150 | 30 | 87 | 13 | 9 | 82 | 18 | | | | 5 | 37 | 63 |



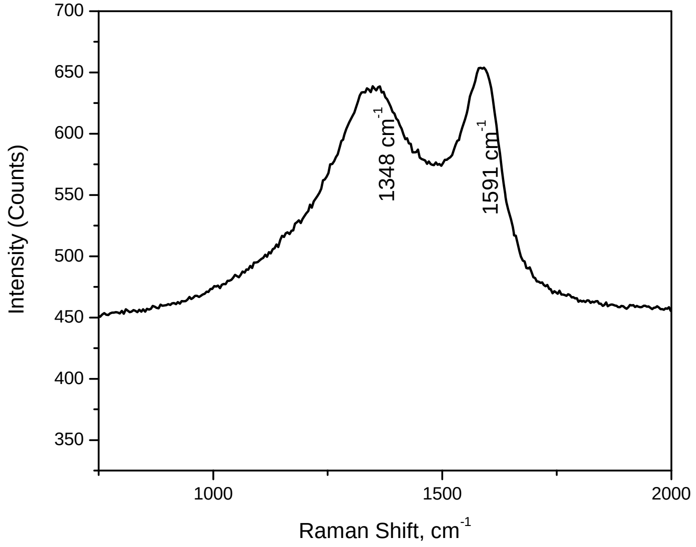


**Effect of Carbon Support on the Hydrogenation activity** **Effect of W precursor on the Hydrogenation activity**

# Activated Carbon from Limonea Acidissima - Structural Properties



**XRD Pattern**



**Raman Spectrum**

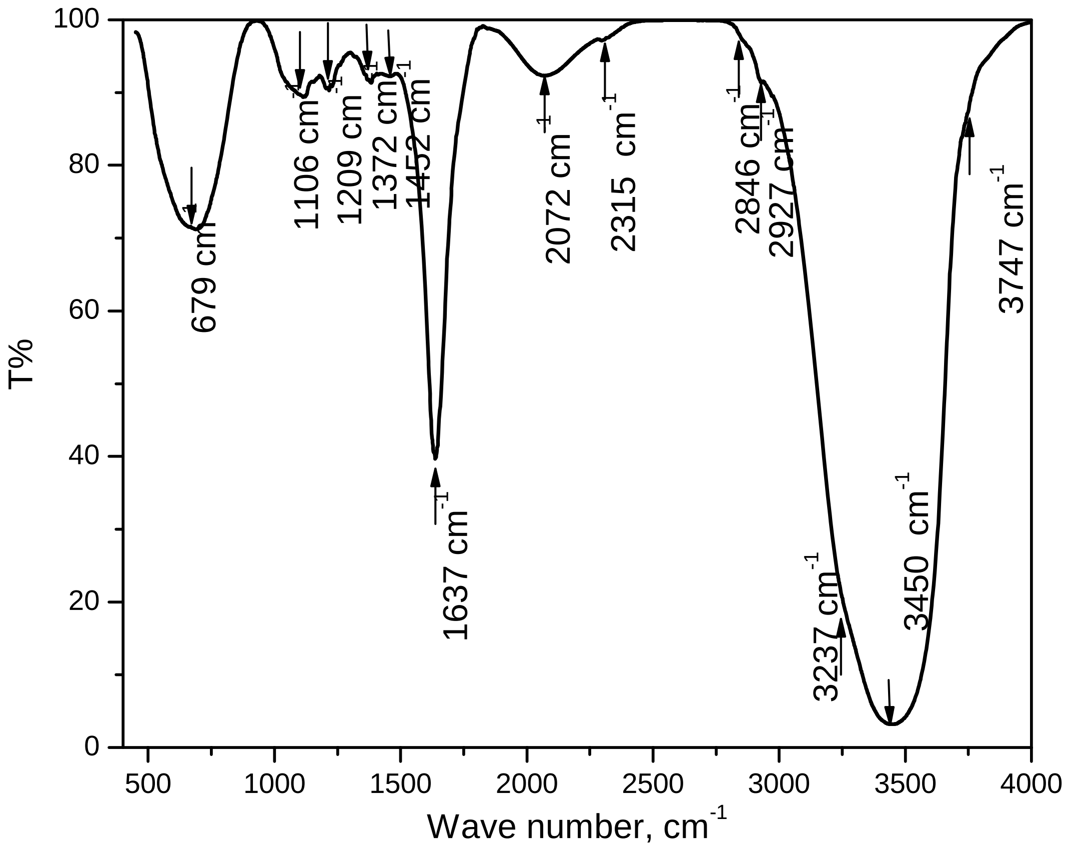
## Crystallographic structural details deduced from XRD studies

| S. No. | Sample | $d_{002}$ (nm) | *$L_c$ (nm) | *$L_a$ (nm) |
|---|---|---|---|---|
| 1 | Activated Carbon, $C_{WA}$ | 0.377 | 1.1 | 3.656 |

## Structural parameters deduced from the confocal Raman spectroscopic studies

| S. No. | Sample | Peak Intensity Frequency, $\nu_x$, cm$^{-1}$ | | $R = I_D/I_G$ | $L_a$ (nm) = 4.4/R (From Raman) | $L_a$ (nm) (from XRD) |
|---|---|---|---|---|---|---|
| | | G band | D band | | | |
| 1 | $C_{WA}$ | 1591 | 1348 | 1.408 | 3.125 | 3.656 |

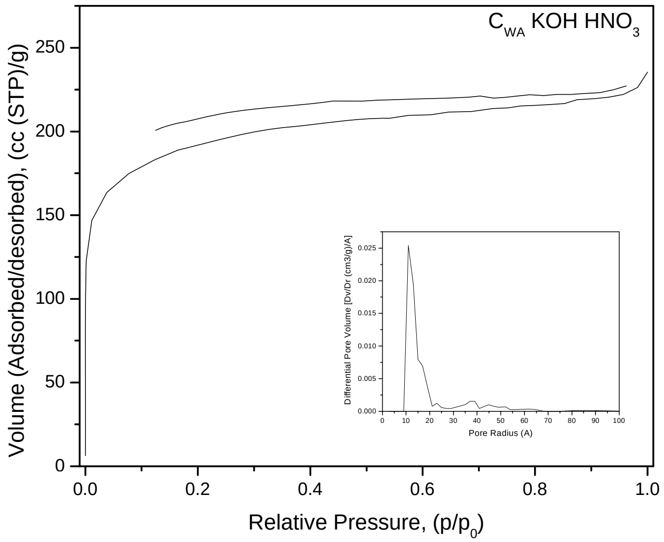
# Activated Carbon from Limonea Acidissima – Surface Functionality



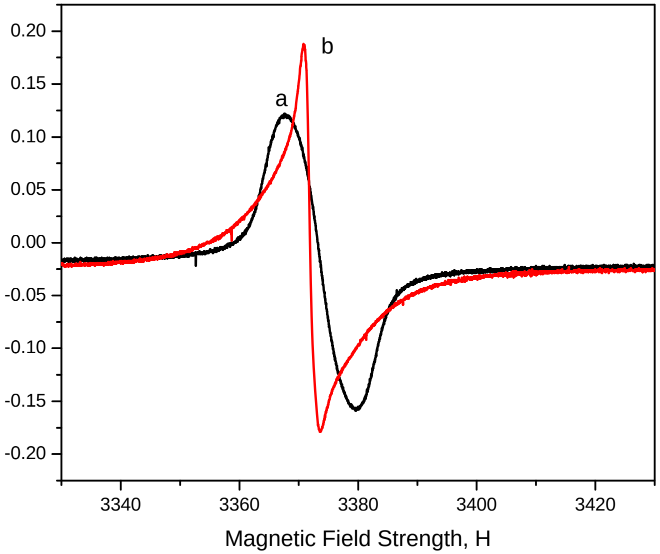
FT – IR spectrum of Activated Carbon (KOH activation)

| **Band position v, cm$^{-1}$** | **Assignment** |
|---|---|
| 3747 | Isolated –OH groups |
| 3450 | O-H stretching vibration of surface hydroxyl groups and adsorbed water. Asymmetry (shoulder like feature at 3237 cm$^{-1}$) indicated presence of hydrogen bonding interaction |
| 2927 | Aliphatic, asymmetric C-H stretching vibration of methylene group |
| 2846 | Aliphatic, symmetric C-H stretching vibration of methylene group |
| 2315 | Ketone group |
| 1637 | C=O (carbonyl) stretching vibration in quinone |
| 1452 | In plane bending vibration of C-H of methylene group |
| 1372 | In plane bending vibration of C-H in methyl group |
| 1000 - 1300 | C-O stretching in phenols, alcohols, acids, ethers and esters |
| 679 | Out of plane deformation vibration of C-H groups located at the edges of aromatic planes |

# Activated Carbon from Limonea Acidissima
# Textural Properties and Electron Spin Density



**$N_2$ adsorption-desorption isotherm and pore size distribution curve**



**EPR spectrum of (a) Activated Carbon from Limonea Acidissima and (b) DPPH**

## Textural Properties deduced from Isotherm

| S. No. | Sample | $S_{BET}$ ($m^2$/g) | $V_P$ ($cm^3$/g) | Mean Pore Diameter$^{i}$ (nm) |
|---|---|---|---|---|
| 1 | Activated carbon, $C_{WA}$ | 698 | 0.35 | 2.0 |

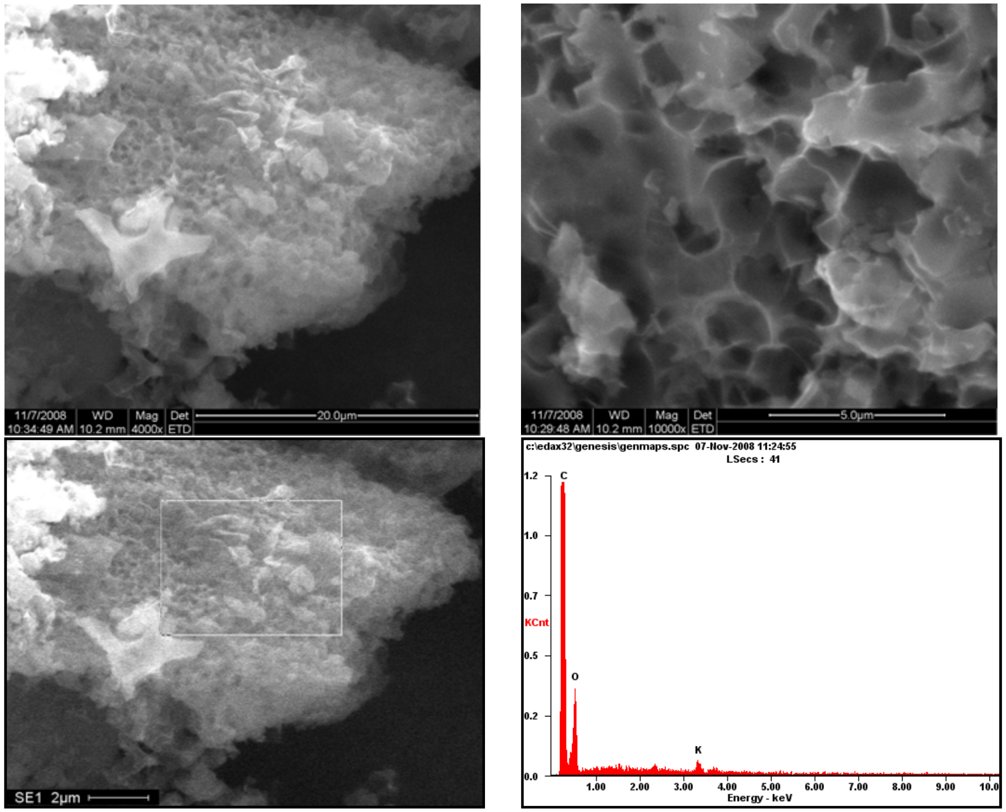
## Electron Spin Concentration deduced from Isotherm

| S. No. | Carbon Material | g-factor value | ΔH (in Gauss) Peak to peak separation | Spin Concentration per gram of carbon material |
|---|---|---|---|---|
| 1 | $C_{WA}$ | 2.03095 | 12 | $0.13 \times 10^{19}$ |

# Activated Carbon from Limonea Acidissima – Morphology and Composition

**4000 x**

**10, 000 x**



SEM images and EDAX spectrum

## The elemental composition from EDAX

| S. No. | Element | Wt. % | At. % |
|---|---|---|---|
| 1 | Carbon | 74.84 | 80.02 |
| 2 | Oxygen | 24.70 | 19.83 |
| 3 | Potassium | 0.45 | 0.15 |

- Ash content – 1.04%

# Activated Carbon from Limonea Acidissima – Catalyst (Pt) Support

**Catalyst Preparation:** Dry impregnation

**7.7 mM $H_2PtCl_6$ $6H_2O$**

↓

**Carbon Support**

↓ **RT, Stirring 12 h**

**$Pt^{4+}$ impregnated Carbon**

↓

**$Pt^{4+}$ impregnated Carbon**

↓ **Reduction, $H_2$, 450 °C, 8 h**

**Pt/C**

## Evaluation of Electrocatalytic Activity of Pt/C catalysts:

**Reaction studied:** **MeOH electrooxidation**

$$CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6\,e^- \qquad E_0 = 0.046\ V$$

## Objective:

i. **Increase Pt utilization**
ii. **Produce active, stable and CO tolerant electrocatalyst**

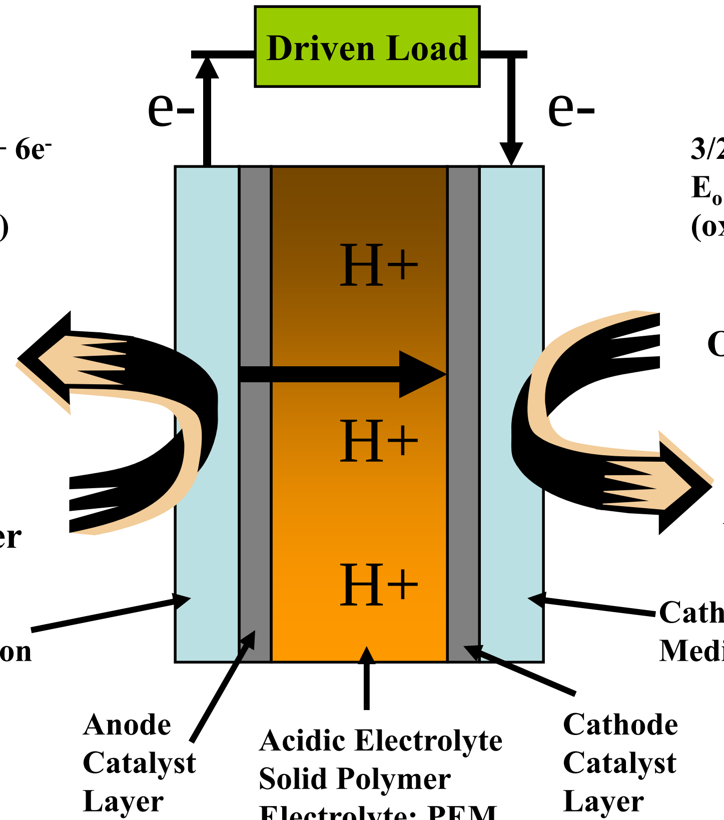
# Direct Methanol Fuel Cell (DMFC)

**Anode**

$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$
$E_o = 0.046$ V
(electro-oxidation of methanol)

**Cathode**

$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
$E_o = 1.23$ V
(oxygen reduction)



Acidic Electrolyte Solid Polymer Electrolyte: PEM (Proton Exchange Membrane)

Nafion 117

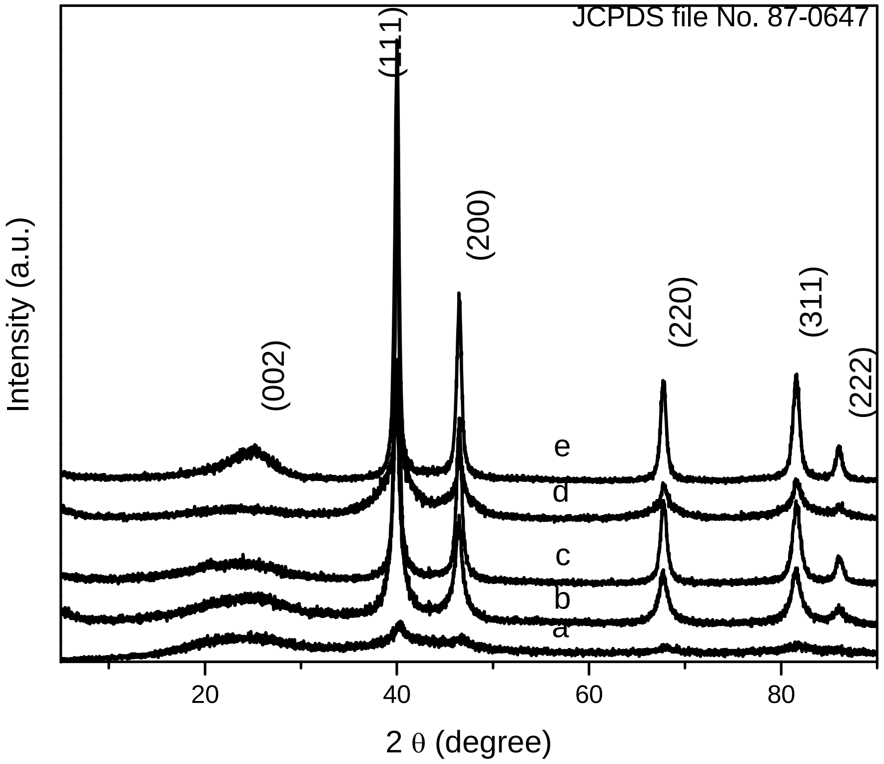
- Reduction of the expensive Pt metal loading
- Enhancement of the long term stability of the electrode
- Improving the CO tolerance of the electrode

## Overall Reaction

$CH_3OH + 3/2\ O_2 + H_2O \rightarrow CO_2 + 3H_2O \quad E_{cell} = 1.18$ V

- Acidic electrolytes are usually more advantageous compared to basic electrolytes
- Acidic electrolytes aid $CO_2$ rejection
- Insoluble carbonates are formed in alkaline electrolytes

# Dispersion of Pt crystallites on Carbon Support

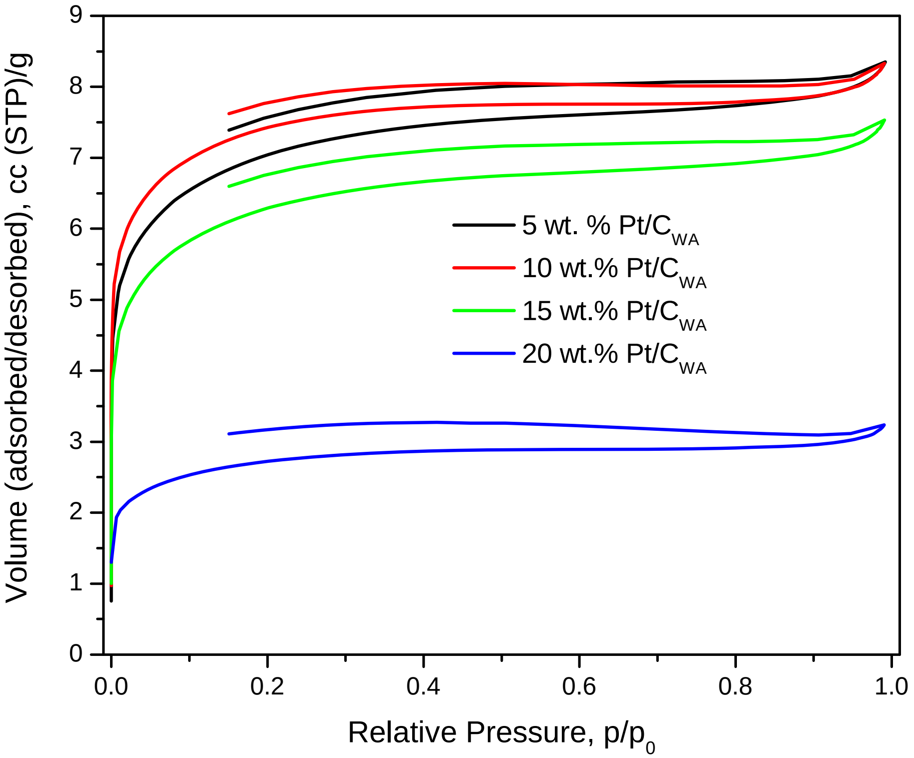


- ❖ Diffraction peaks characteristic of Pt metal with a face centered cubic lattice
- ❖ The lattice constant value of around 0.39 nm correlated well with the FCC structure of Pt metal
- ❖The reflection from (220) plane of Pt metal is considered for the calculation of crystallite size
- ❖ The crystallite size of Pt is found to be dependent on the Pt loading and also on the nature of the carbon support

**X-ray diffraction patterns of (a) 5 wt.% Pt/CWA (b) 10 wt.% Pt/CWA (c) 15 wt.% Pt/CWA and (d) 20 wt.% Pt/CWA and (e) 20 wt.% Pt/Vulcan XC 72 R**

| Catalyst | Crystallite size (nm) | Lattice constant, a, (nm) |
|---|---|---|
| 5 wt. % Pt/CWA | 5.0 | 0.3897 |
| 10 wt. % Pt/CWA | 10.2 | 0.3909 |
| 15 wt. % Pt/CWA | 13.5 | 0.3907 |
| 20 wt. % Pt/CWA | 10.4 | 0.3904 |
| 20 wt.% Pt/Vulcan XC 72 | 13.1 | 0.3909 |

# Textural Properties of Pt/C Electrocatalysts



**$N_2$ adsorption-desorption isotherms of $Pt/C_{WA}$ electro catalysts**
**(a) 5 wt.% $Pt/C_{WA}$, (b) 10 wt.% $Pt/C_{WA}$ (c) 15 wt.% $Pt/C_{WA}$ and (d) 20 wt. % $Pt/C_{WA}$**

| S. No. | Electro catalyst | $S_{BET}$ $(m^2/g)$ | $^{i}S_{Micropore}$ $(m^2/g)$ | $^{ii}V_P$ $(cm^3/g)$ | Mean Pore Diameter$^{iii}$ (nm) |
|---|---|---|---|---|---|
| 1 | 5 wt. % $Pt/C_{WA}$ | 505 | 267 | 0.289 | 2.28 |
| 2 | 10 wt. % $Pt/C_{WA}$ | 526 | 318 | 0.288 | 2.19 |
| 3 | 15 wt. % $Pt/C_{WA}$ | 451 | 233 | 0.261 | 2.31 |
| 4 | 20 wt. % $Pt/C_{WA}$ | 195 | 102 | 0.119 | 2.44 |

# Electrochemical Measurements

**Electrode Fabrication:**

**Catalyst (Pt/C) dispersed in distilled water**
**20 mg/ml**

↓

**Ultrasonicated for 10 min**

↓

**10 µlit ink pipetted onto the GC disk**

↓ Dried in air oven at 60 °C

**5 µlit nafion pipetted onto the catalyst deposited on the GC disk**

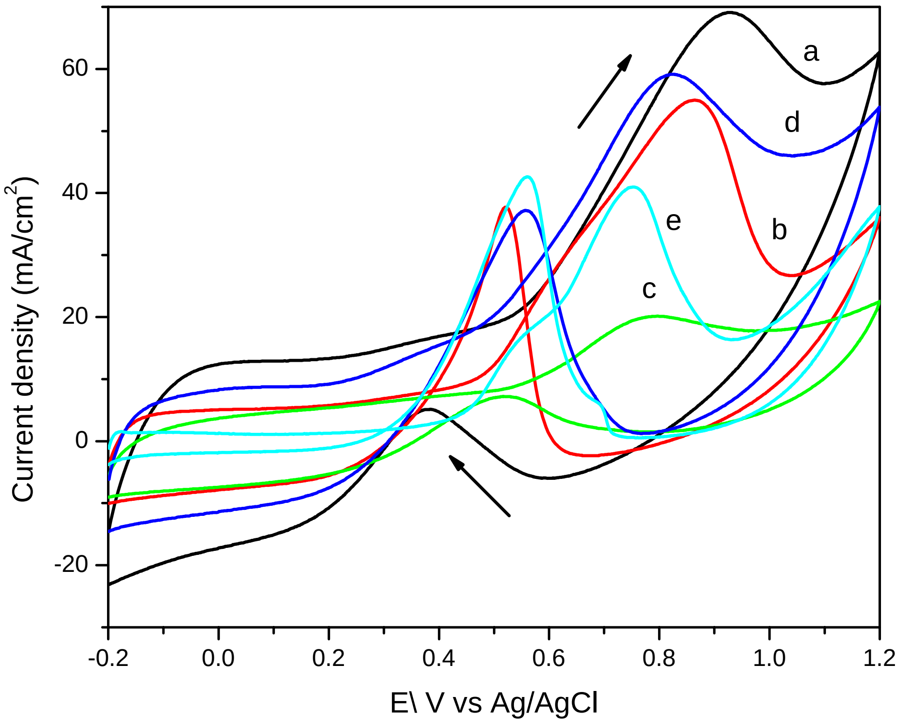
↓ Dried at room temperature

**GC/Carbon- Pt - Nafion electrode**

**Experimental Conditions:**

**Electrolyte : 0.5 M $H_2SO_4$**
**Working Electrode : Pt/C catalyst deposited on GC disk**
**Reference Electrode : Ag/AgCl, 3.5 M KCl (+ 0.205 V Vs NHE)**
**Counter Electrode : Pt foil (1.5 $cm^2$)**
**Scan rate : 5, 10, 15, 20 and 25 mV/sec**

# MeOH Electrooxidation Activity of Pt/C catalysts

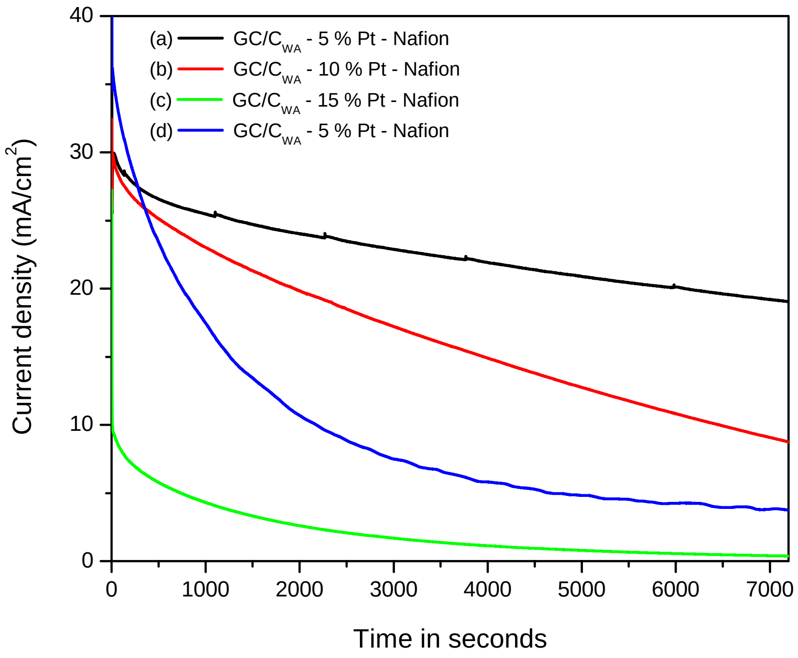


**Cyclic Voltammetric response of**
**(a) GC/C$_{WA}$ - 5 wt.% Pt - Nafion electrode**
**(b) GC/C$_{WA}$ - 10 wt.% Pt - Nafion electrode**
**(c) GC/C$_{WA}$ - 15 wt.% Pt - Nafion electrode and**
**(d) GC/C$_{WA}$ - 20 wt.% Pt - Nafion electrode and**
**(e) GC/Vulcan XC 72 R - 20 wt.% Pt - Nafion electrode in 0.5 M $H_2SO_4$ and 1 M MeOH, at a scan rate of 25 mV/sec between -0.2 to 1.2 V Vs Ag/AgCl**

## Comparison of Electrocatalytic Activity – Pt/C$_{WA}$ and Pt/Vulcan XC 72 R

| S. No. | Electrode | Onset Potential, V | $i_f/i_b$ | Activity* | | | |
|---|---|---|---|---|---|---|---|
| | | | | Forward sweep | | Reverse sweep | |
| | | | | I (mA/cm$^2$) | E (V) | I (mA/cm$^2$) | E (V) |
| 1 | GC/C$_{WA}$-5 % Pt-Nafion | 0.21 | 14.4 | 69.0 | 0.92 | 4.97 | 0.37 |
| 2 | GC/C$_{WA}$-10 % Pt-Nafion | 0.18 | 1.45 | 55.0 | 0.86 | 37.6 | 0.52 |
| 3 | GC/C$_{WA}$-15 % Pt-Nafion | 0.30 | 2.76 | 20.0 | 0.79 | 7.2 | 0.51 |
| 4 | GC/C$_{WA}$-20 % Pt-Nafion | 0.18 | 1.60 | 58.9 | 0.82 | 37.28 | 0.51 |
| 5 | GC/Vulcan XC 72 R-20 % Pt-Nafion | 0.25 | 0.96 | 40.9 | 0.75 | 42.6 | 0.56 |

# Electrochemical Stability of Pt/C catalysts - Chronoamperometry

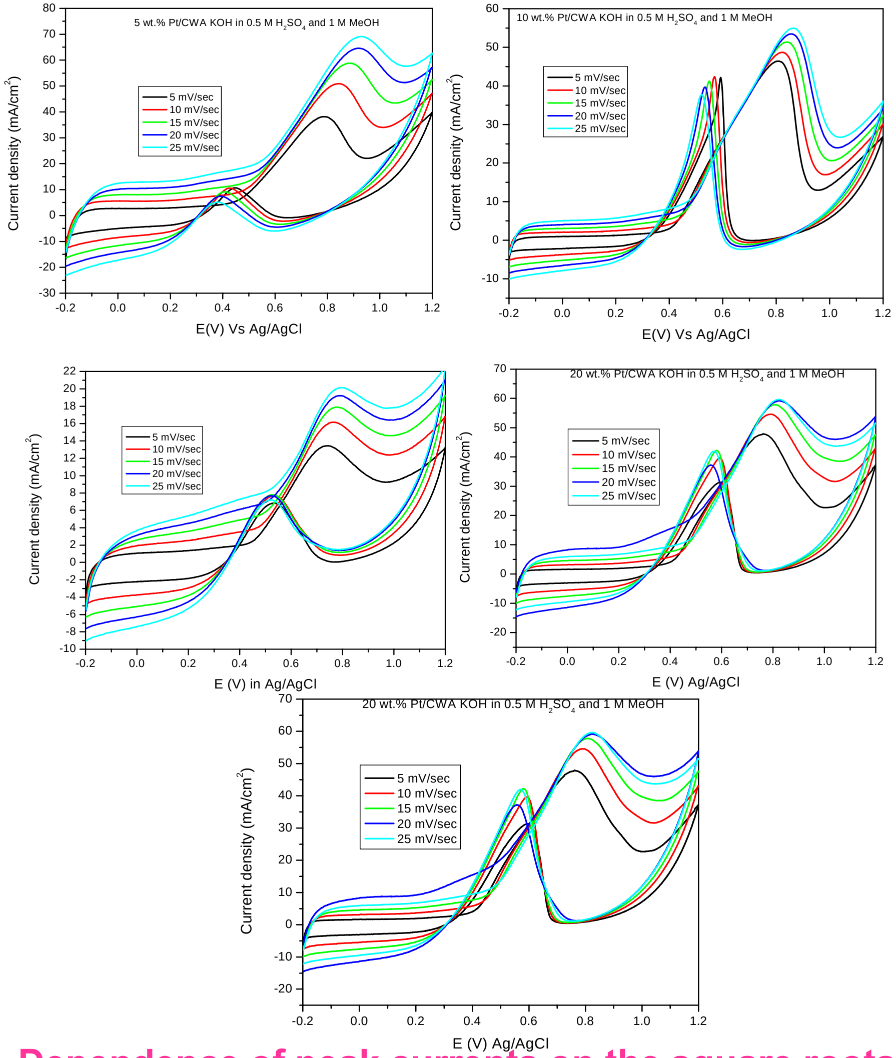


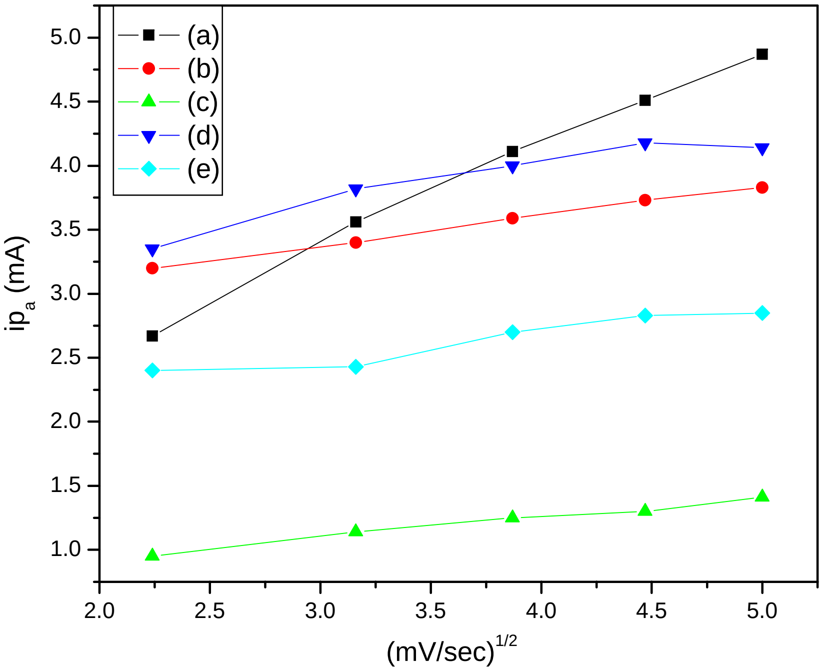
Chromoamperometric response of
(a) GC/C$_{WA}$ - 5 wt.% Pt - Nafion electrode
(b) GC/C$_{WA}$ - 10 wt.% Pt - Nafion electrode
(c) GC/C$_{WA}$ - 15 wt.% Pt - Nafion electrode and
(d) GC/C$_{WA}$ - 20 wt.% Pt – Nafion electrode
polarized at + 0.6 V Vs Ag/AgCl
in 0.5 M $H_2SO_4$/ 1 M MeOH for 3 hours

| S. No. | Electrode | Activity* | | % Decrease in activity after 3 hs at + 0.6 V |
|---|---|---|---|---|
| | | Initial (I), mAcm$^{-2}$ | Final (I), mAcm$^{-2}$ | |
| 1 | GC/C$_{WA}$-5 % Pt-Nafion | 25.2 | 19.1 | 24 |
| 2 | GC/C$_{WA}$-10 % Pt-Nafion | 29.7 | 19.0 | 36 |
| 3 | GC/C$_{WA}$-15 % Pt-Nafion | 10.0 | 0.4 | 96 |
| 4 | GC/C$_{WA}$-20 % Pt-Nafion | 36.1 | 3.7 | 89 |

*Stability evaluated in 0.5 M $H_2SO_4$ and 1 M $CH_3OH$ for 3 h with the electrode being polarized at + 0.6 V Vs Ag/AgCl

# Effect of Scan Rate on Current response of GC/Carbon- Pt – Nafion electrode





**Current Vs Sq. root of Scan Rate**

**Dependence of peak currents on the square roots of scan rates for**

**(a) GC/Pt CWA 5 wt.%- Nafion electrode, (b) GC/Pt CWA 10 wt.%- Nafion electrode,**

**(c) GC/Pt CWA 15 wt.%- Nafion electrode, (d) GC/Pt CWA 20 wt.%- Nafion electrode**

**(d) and (e) GC/Pt Vulcan XC 72 20 wt.% - Nafion electrode in 0.5 M $H_2SO_4$ and 1 M MeOH,**

**(e) at different scan rates (5, 10, 15, 20 and 25 mV/sec) between -0.2 to 1.2 V Vs Ag/AgCl**

- **Current varied linearly as a function of sq. root of scan rate**
- **MeOH electrooxidation on Pt/C catalysts is diffusion controlled**

## Summary:

- Limonea Acidissima Shells are suitable precursor for producing activated carbon
- KOH activation followed by HNO3 treatment resulted in high specific surface area carbon material (698 $m^2/g$)
- Quinone type carbonyl (C=O) functional groups are formed on the surface of the carbon upon activation with KOH followed by $HNO_3$ treatment
- Significant amount of unpaired electron spins ($0.13 \times 10^{19}$ spins/g) with g value (2.03095) close to free electron g value are observed. The spin concentration values are comparable with those of commercial acetylene black (3.8 x 1019) and graphon (1.1 x 1019).
- The activated carbon material produced from Limonea Acidissima by KOH activation is a suitable support for Pt for the electroxidation of MeOH
- The excellent performance of 5 wt. % Pt/$C_{WA}$ is attributed to the increase in the extent of utilization of Pt metal because of the smaller crystallite size of Pt (5 nm)
- The use of carbon material from Limonea acidissima as support for Pt offered the promise of effective utilization of Pt, higher electrooxidation (MeOH) activity and CO tolerance compared to 20 wt.% Pt/Vulcan XC 72 R prepared under identical conditions
- Pt/CWA catalysts showed improved CO tolerance compared to Pt/Vulcan XC 72 R
- With the same amount of Pt loading (20 wt.%) the crystallite size of Pt on CWA support is smaller (10.4 nm) compared to the crystallite size (13.1 nm) on Vulcan XC 72 R (commercial fuel cell grade carbon support)
- Carbon material from the inexpensive and abundant source of wood apple shells can be a substitute of commercial fuel cell grade carbon

# IV. Activated Carbon from Borassus Flabellifera (ACBF)

Common Names : Palmyra palm, Toddy palm, wine palm, Talauriksha palm
Distribution : India, Srilanka

## Synthesis
## Characterization
## Application as Catalyst (HPW & Pt) support

Flower Spikes

↓

Combustion in limited supply of air at 300 ºC in a muffle furnace

↓

Coal ground

↓

Sieved through 200 mesh

↓

Impregnation with Activating Agent

↓

Heat treatment, 800 ºC, 8 h, $N_2$ atm

↓

Treatment with HCl, carbon : acid = 1:10, wt./vol. 8h

↓

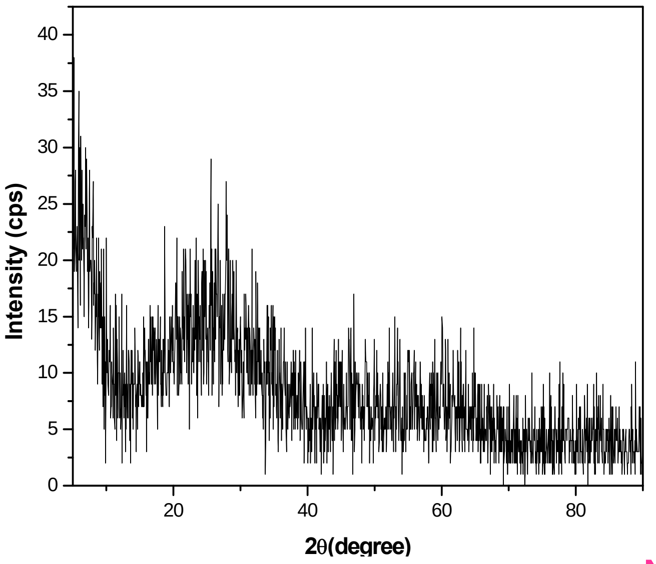
Filtered, washed with distilled water, Air dried and oven dried at 150 ºC

↓

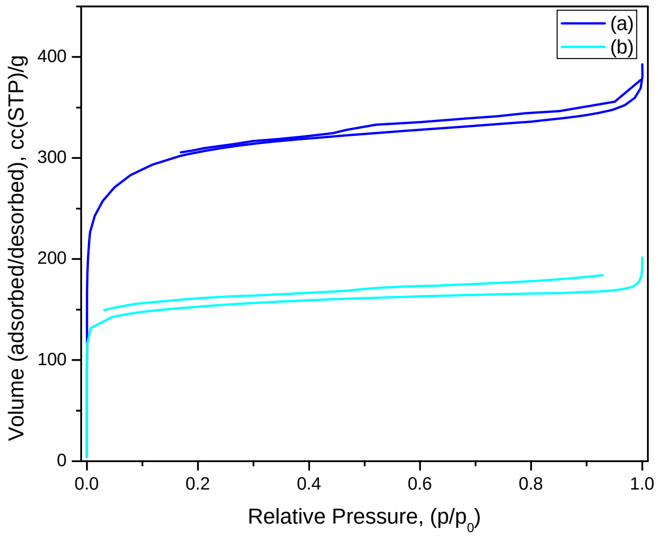
Activated carbon

B. Viswanathan, T. K. Varadarajan, P. Indra Neel, Patent No. IN 2007 CH00376

# Activated Carbon from Borassus Flabellifera
# Structural, Textural and Morphological Properties

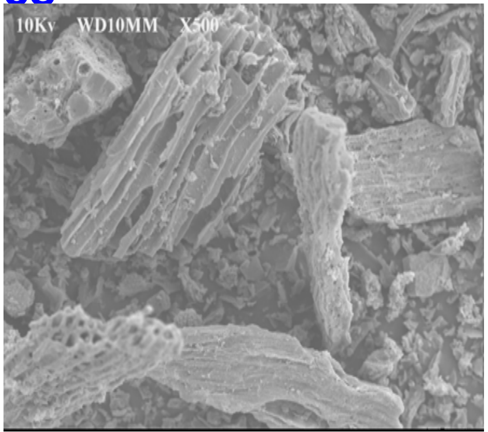


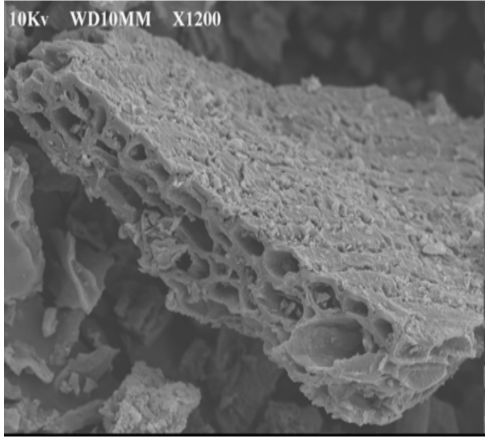
**XRD pattern of Activated Carbon**



**$N_2$ adsorption-desorption isotherms of (a) activated carbon with a Char:$K_2CO_3$ (wt./wt.%) = 1:1 of (b) Thermal activated carbon (800 °C, 8 h, Ar atm.**

(a) 500 x

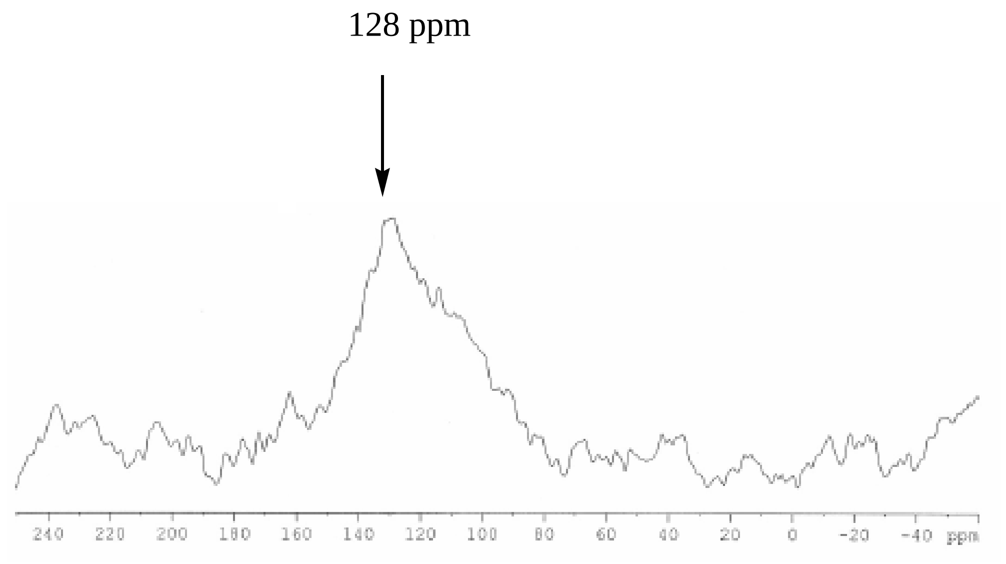




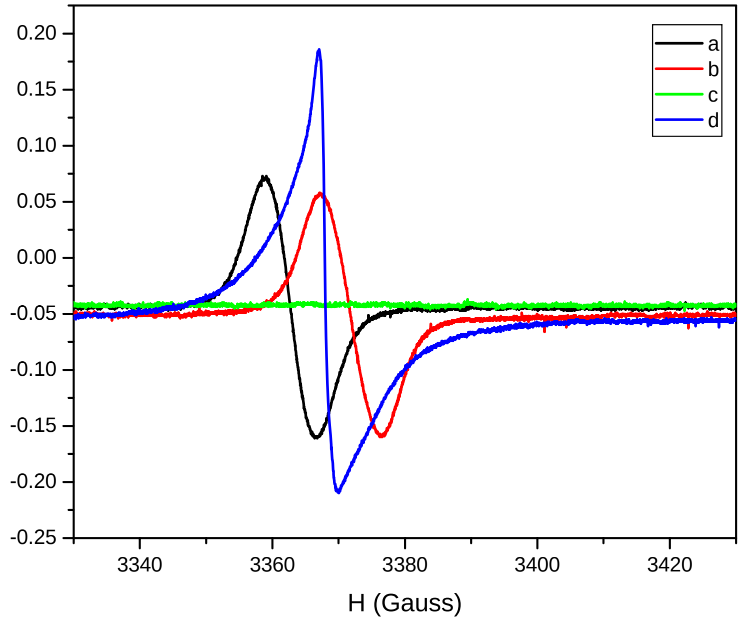
(b) 1200 x

| S. No. | Sample | $K_2CO_3$ : C (wt./wt.%) | $S_{BET}$ ($m^2/g$) | $V_P$ ($cm^3/g$) | Mean Pore Diameter$^{ii}$ (nm) |
|---|---|---|---|---|---|
| 1 | Char | 0 | 17 | 0.07 | 10.0 |
| 2 | Activated with $K_2CO_3$ | 1 | 1070 | 0.55 | 2.0 |
| 3 | Thermal Activated | 0 | 550 | 0.28 | 2.0 |

# Carbon Materials from Borassus Flabellifera – $^{13}$C MAS NMR and EPR studies



$^{13}$C MAS NMR spectrum of the Char

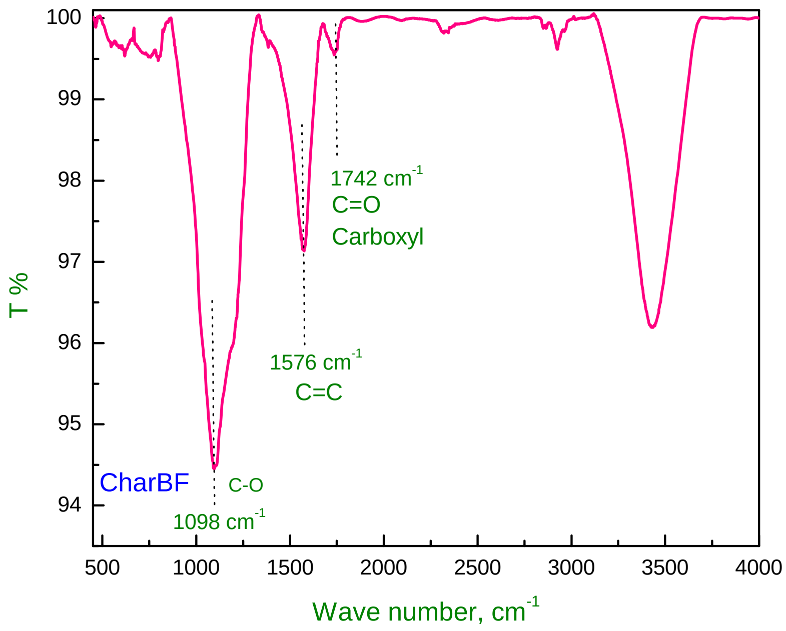


**EPR spectra of (a) char (b) char treated with NaOH and HCl, (c) char activated with $K_2CO_3$ (char:$K_2CO_3$ (wt./wt.%) =1:4) and (d) DPPH**

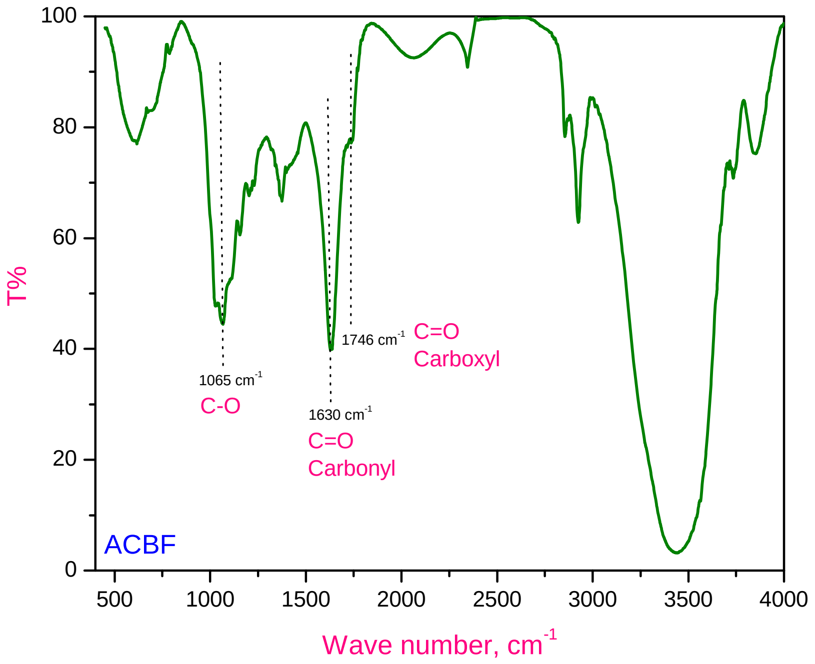
- Strong resonance line near 121 ppm - carbon nuclei in the aromatic planes

| S. No. | Carbon Material | g-factor value | ΔH (in Gauss) Peak to peak separation | Spin Concentration per gram of carbon material |
|---|---|---|---|---|
| 1 | Char (as synthesized) | 2.01033 | 7.5 | $0.62 \times 10^{19}$ |
| 2 | Char (base and acid treated) | 2.01344 | 9.0 | $0.55 \times 10^{19}$ |
| 3 | Char activated with $K_2CO_3$<br>(char:$K_2CO_3$ = 1:4, wt./wt.%) | - | - | - |

# Carbon Materials from Borassus Flabellifera – Surface Functionality



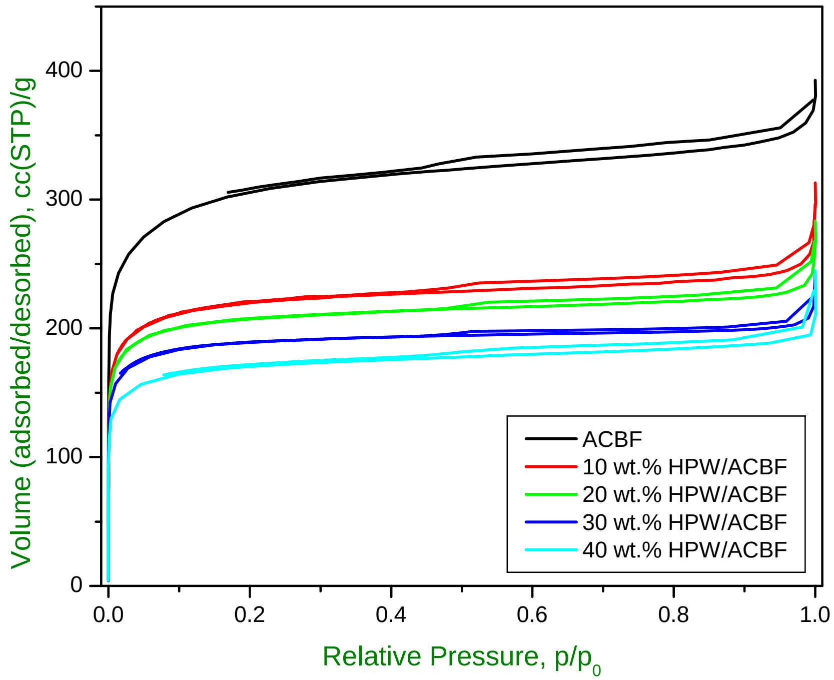
**FT – IR Spectrum of Char**



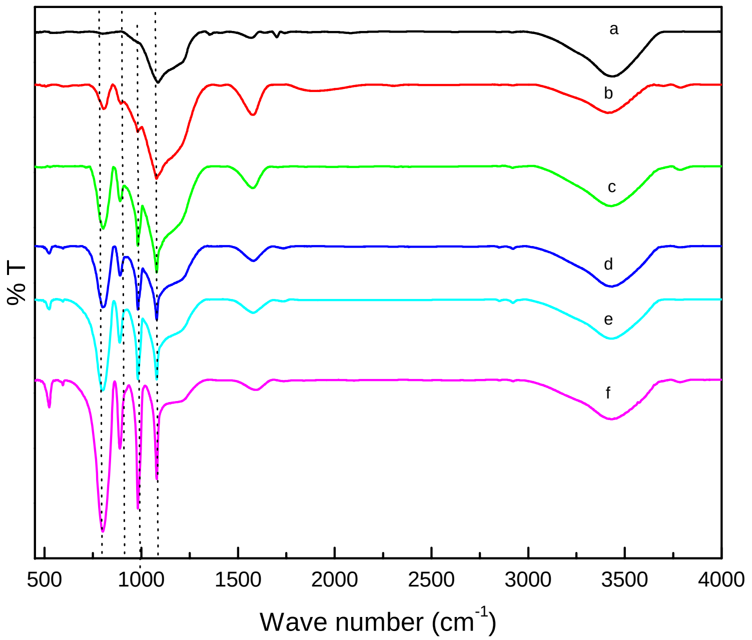
**FT – IR Spectrum Activated Carbon**

- **In the activated carbon C=O (quinone type carbonyl groups) predominated over the C=C stretching in the aromatic ring**
- **This indicates extensive oxidation of carbon surface upon activation with $K_2CO_3$ (Char:$K_2CO_3$ = 1:1)**

# Activated Carbon from Borassus Flabellifera – Support for HPW



$N_2$ adsorption-desorption isotherm for HPW/BFAC



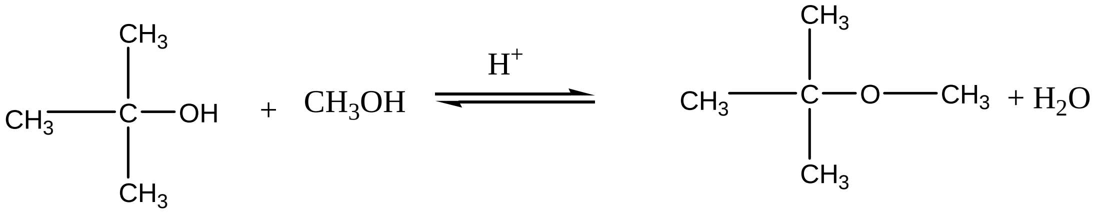
FT – IR spectra of HPW/BFAC

| Catalyst | $S_{BET}$ ($m^2g^{-1}$) | $V_P$ ($cm^3g^{-1}$) |
|---|---|---|
| ACBF | 1070 | 0.5557 |
| 10 wt% HPW/ACBF | 786 | 0.3864 |
| 20 wt% HPW/ACBF | 756 | 0.3609 |
| 30 wt% HPW/ACBF | 678 | 0.3133 |
| 40 wt% HPW/ACBF | 582 | 0.2916 |

| Band Position, ν, $cm^{-1}$ | | Assignment |
|---|---|---|
| Bulk HPW | HPW/ACBF | |
| 1080 | 1072 - 1091 | P-O |
| 983 | 964 - 988 | W=$O_t$ |
| 889 | 895 - 910 | W-O-$W_c$ |
| 839 | 795 - 819 | W-O-$W_e$ |

# Activated Carbon from Borassus Flabellifera – Support for HPW

## Application of HPW/ACBF Catalysts – Vapour Phase Synthesis of MTBE



## MTBE - Special Features

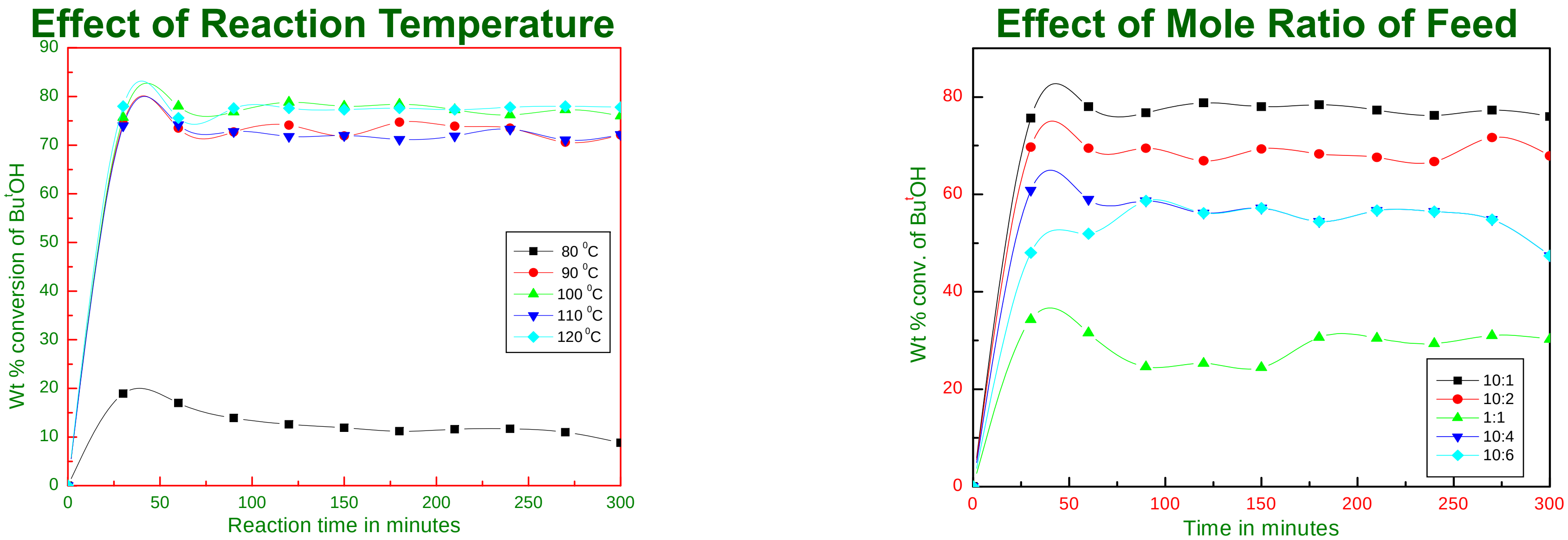
### Highly favourable performance qualities

High octane number
Low sulfur content
Acceptable blending vapour pressure
High miscibility in gasoline
Moderate boiling point
Stability in storage
Cost comparable to other high-octane component
Economical choice in the refinery market place
Preferred over several gasoline oxygenates including DIPE, TAME and ETBE

### Reaction conditions :

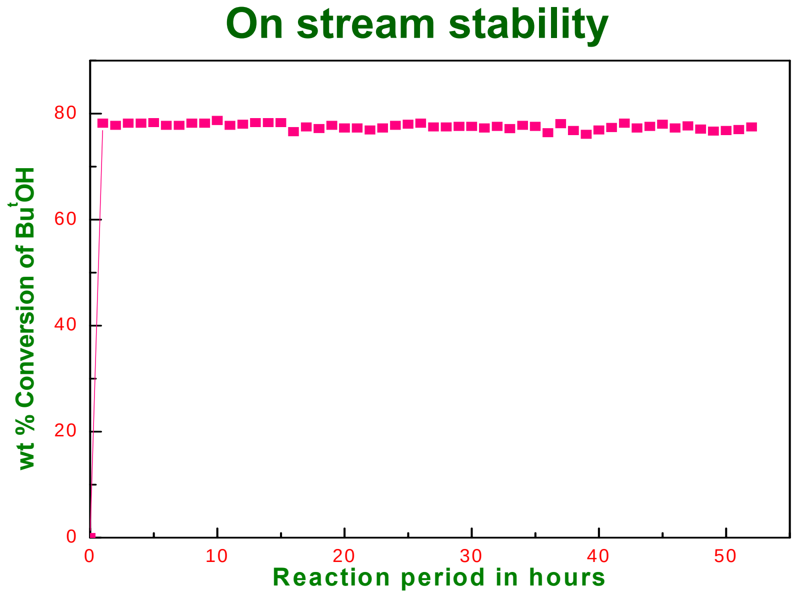
Catalyst employed : 20 wt % HPW/ACBF
Amount of catalyst : 0.5 g
Reaction temperatures employed :
80, 90, 100, 110, 120 °C
Flow rate of the feed : 10 ml/h
Flow rate of carrier gas : 30 ml/h
MeOH : t BuOH = 10 : 1, 10:2, 10:4, 10:6, 1:1
(mole ratio)

# HPW/ACBF - MTBE synthesis


Effect of Reaction Temperature

Effect of Mole Ratio of Feed

% conv. of Bu$^{t}$OH Vs reaction time (in minutes)


On stream stability

% conv. of Bu$^{t}$OH Vs reaction time (in hours)

- ➢ **Optimum reaction temperature - 100 °C**
- ➢ **Optimum mole ratio of feed (MeOH:tert butanol) - 10:1**
- ➢ **Exhibited on stream stability for 50 h**
- ➢ **HPW/ACBF is a potential catalyst for MTBE synthesis**

# Carbon Vs Silica – A comparison of support performance

## Synthesis of SBA-1 Mesoporous silica

Molar composition : 1 TEOS : 0.2 Surfactant : 56 HCl : 700 $H_20$

**CTAB ( 3.494 g ) + $H_2O$ ( 600 ml)**

↓ 82 ml HCl, Temp. 273 K, Slow stirring

**TEOS ( 10.7 ml)**

↓ Solution Stirredfor 8 h, Temp. 273 K

**Gel**

↓ Aged for 2 days; Filtered, Vacuum dried,
Oven dried at 423 K

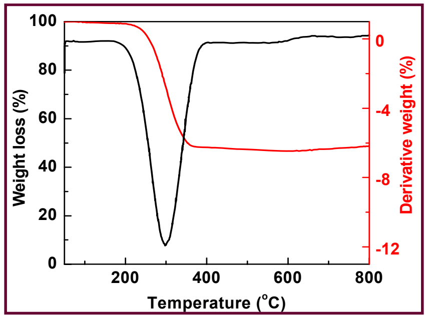
↓ Washed with a solution of EtOH : HCl : $H_2O$ mixture

↓ Air dried at 373 K for 3 h

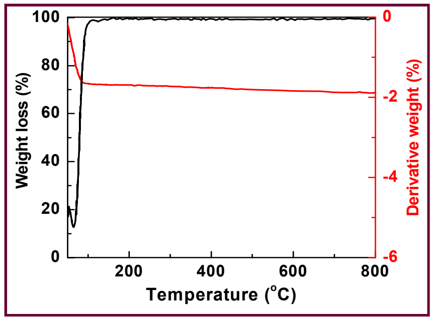
**SBA-1 as-synthesised**

↓ Calcined in Ar atm at 873 K for 1 h and in air for 6 h

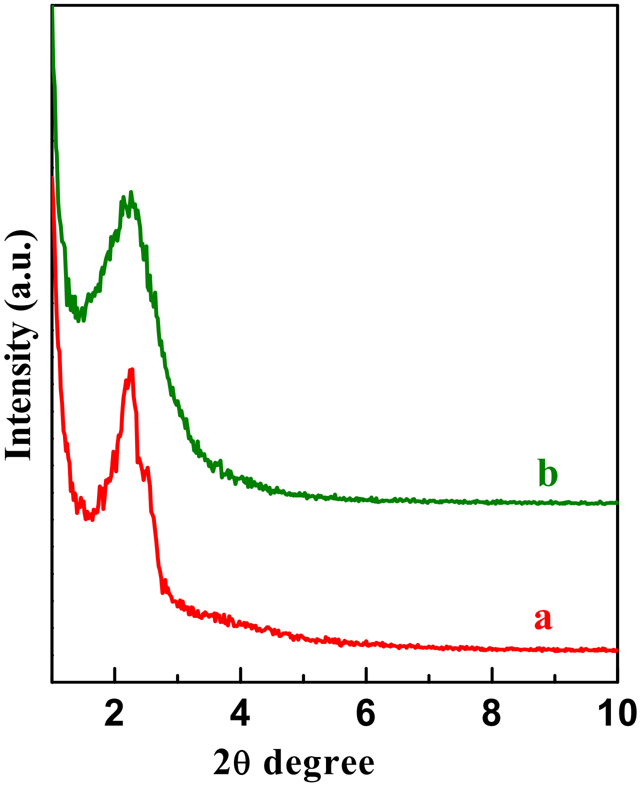
**SBA- 1 calcined**



As-synthesised

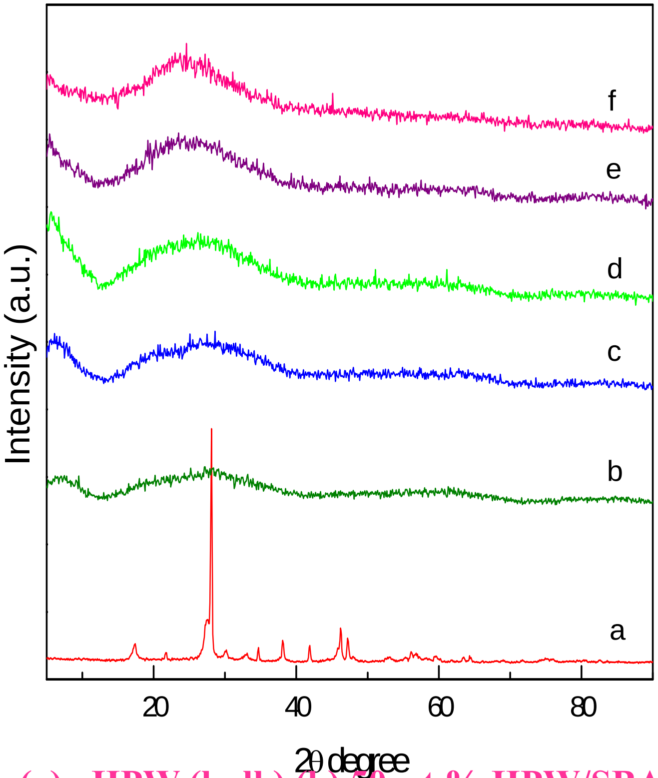


Calcined

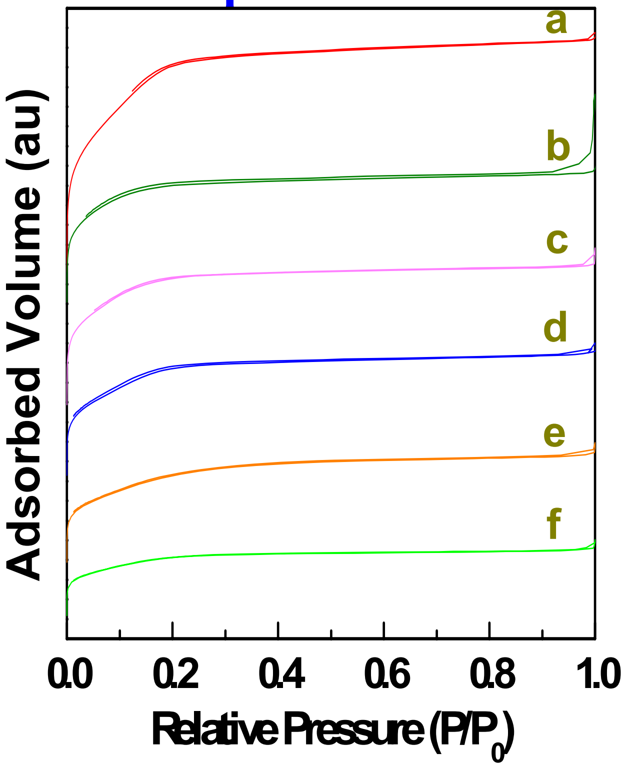


XRD pattern of SBA-1
(a) Calcined (b) As-synthesised

# HPW/SBA-1 - Textural and Structural Properties



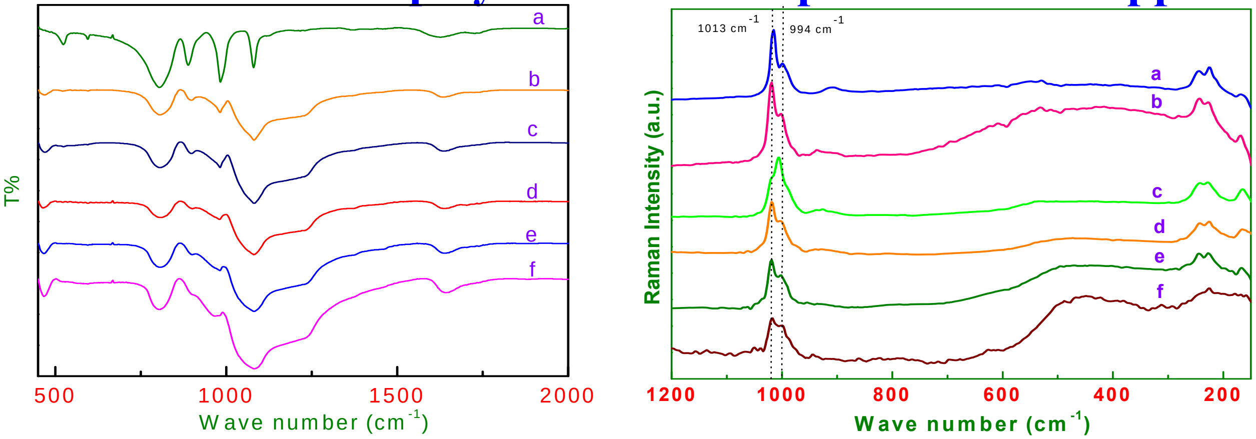
(a) HPW (bulk) (b) 50 wt % HPW/SBA-1
(c) 40 wt % HPW/SBA-1 (d) 30 wt % HPW/SBA-1
(e) 20 wt % HPW/SBA-1 (f) 10 wt % HPW/SBA-1



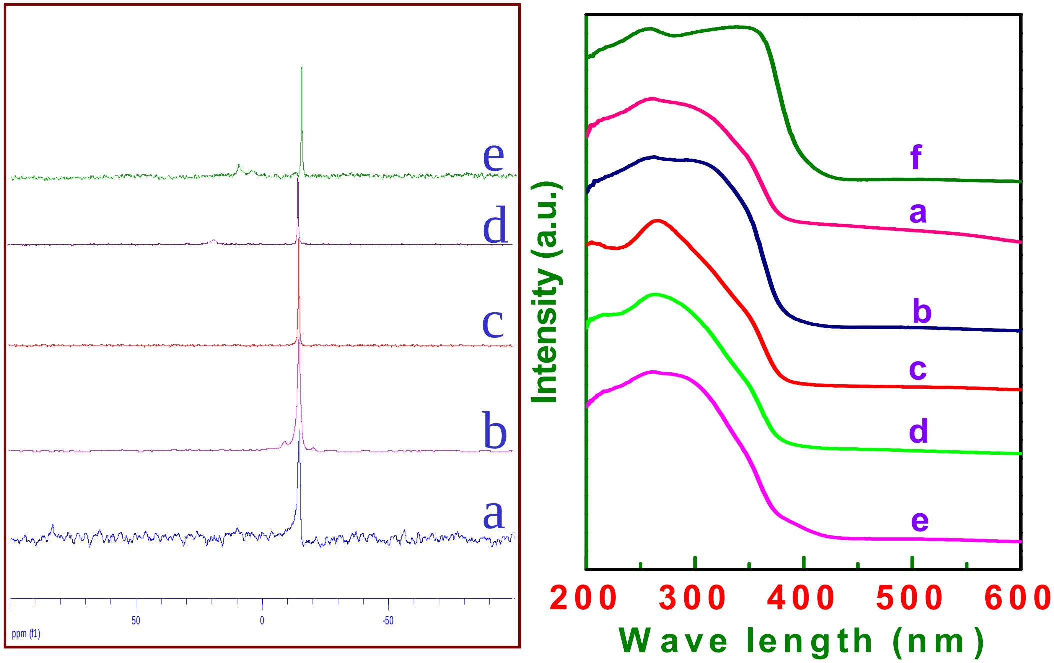
(a) SBA-1 calcined (b) 10 wt % HPW/SBA-1
(c) 20 wt % HPW/SBA-1 (d) 30 wt % HPW/SBA-1
(e) 40 wt % HPW/SBA-1 (f) 50 wt % HPW/SBA-1

| Catalyst | $S_{BET}$ ($m^2g^{-1}$) | $V_P$ ($cm^3g^{-1}$) |
|---|---|---|
| SBA-1 calcined | 918 | 0.4621 |
| 10 wt % HPW/SBA-1 | 567 | 0.2803 |
| 20 wt % HPW/SBA-1 | 535 | 0.2601 |
| 30 wt % HPW/SBA-1 | 480 | 0.2441 |
| 40 wt % HPW/SBA-1 | 393 | 0.2210 |
| 50 wt % HPW/SBA-1 | 265 | 0.1472 |

# Structure of Heteropoly acids on Mesoporous Silica Support



FT – IR and FT – Raman Spectra of (a) HPW (bulk) (b) 50 wt % HPW/SBA-1 (c) 40 wt % HPW/SBA-1 (d) 30 wt % HPW/SBA-1 (e) 20 wt % HPW/SBA-1 (f) 10 wt % HPW/SBA-1



$^{31}$P MAS NMR and Diffuse reflectance UV-Visible spectra

(a) 50 wt % HPW/SBA-1

(b) 40 wt % HPW/SBA-1

(c) 30 wt % HPW/SBA-1

(d) 20 wt % HPW/SBA-1

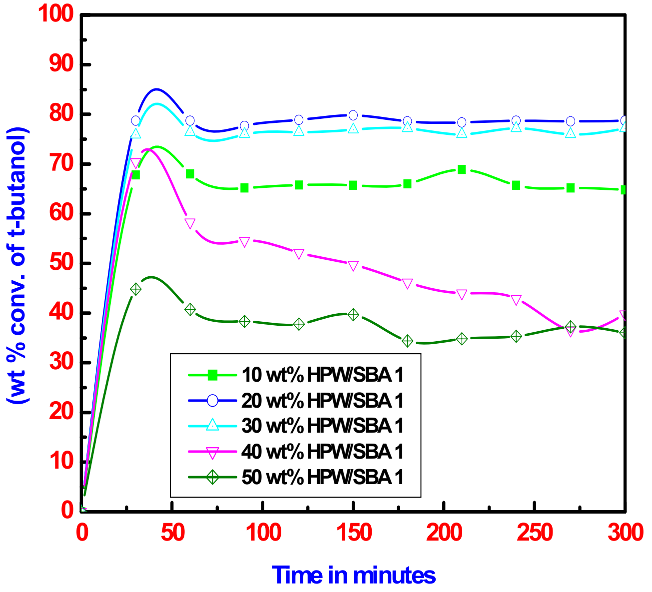
(d) 10 wt % HPW/SBA-1

(f) HPW (bulk)

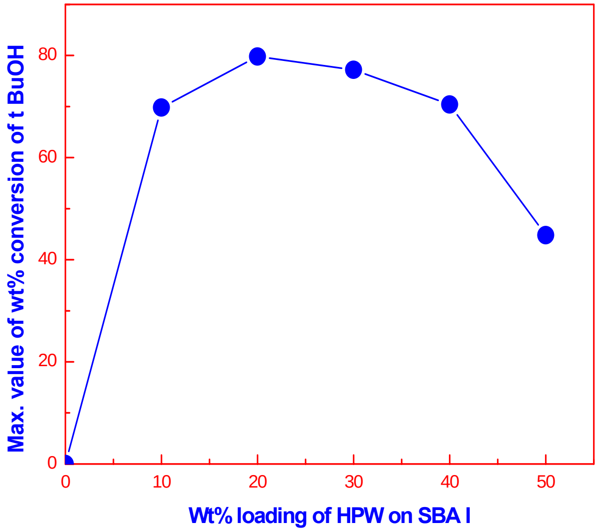
P. Indra Neel, B. Viswanathan, T. K. Varadarajan,
17th National symposium on Catalysis, 18-20th January, 2005, CSMCRI, Bhavnagar, Gujarat, India.

# HPW/SBA-1 Catalysts – MTBE Synthesis

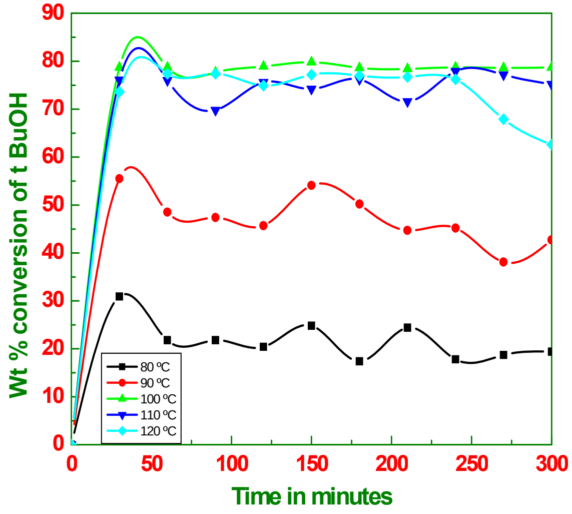
**Effect of wt % loading of HPW on the conversion of t-BuOH**



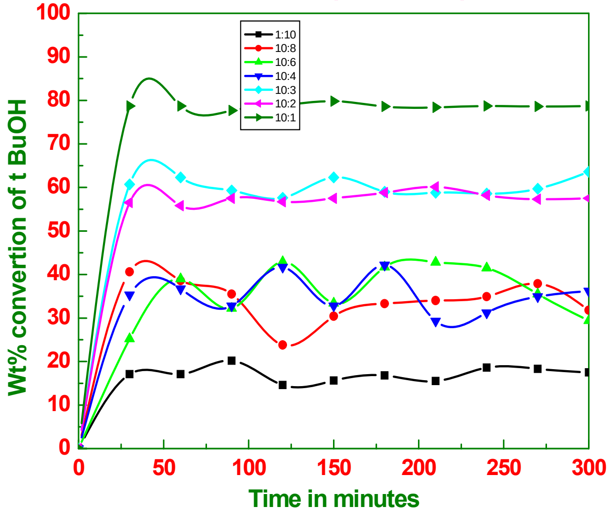
Plot of wt % Conv. of t-BuOH Vs Reaction Time (in min.)



Plot of wt % Conv. of t-BuOH Vs wt % loading of HPW on SBA-1



Plot of wt % conv. of t-BuOH Vs reaction time (in minutes) variation of temp. from 80 to 120 ºC



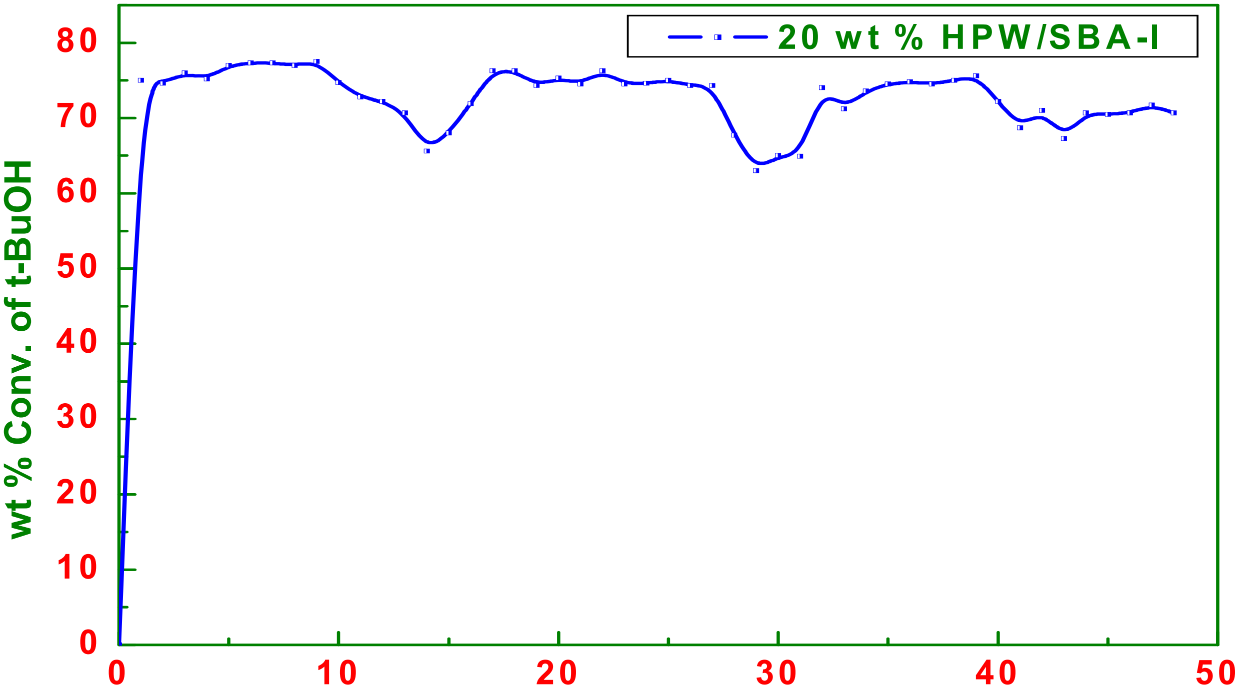
Effect of mole ratio of the feed

- Optimum loading of HPW – 20 wt.%
- Optimum temperature is 100 ºC with a maximum t-BuOH conv. of 80 wt %
- Optimum mole ratio of MeOH : t-BuOH should be 10 : 1
- Optimum flow rate of the feed – 10 ml/h

  Different flow rates of the feed (4, 6, 8, 10, 12 and 14 ml/h) were employed

# Evaluation of on stream stability - HPW/SBA – 1

Reaction temperature = 100 ºC
MeOH : t-BuOH (Mole ratio) =10 : 1
Flow rate of the feed = 10 ml/h
Carrier gas = $N_2$
Flow Rate of carrier gas = 30 ml/h
Catalyst = 20 wt % HPW/SBA-1
Amount of catalyst = 0.5 g



Plot of wt % conv. of t-BuOH Vs reaction time (in hours)

- The catalyst is stable (active and selective) upto 48 h on stream and is expected to perform well even after 48 h

P. Indra Neel, B. Viswanathan, T. K. Varadarajan,
National symposium and conference on Solid state chemistry, 1-3rd December, 2005,
ISCAS-2005, University of Goa, Goa, India

## Summary:

- Flower spikes of Borassus Flabellifera are a promising precursor for activated carbon
- The activated carbon material is amorphous and microporous with tubular pore net work
- Activated carbon from the natural source is an appropriate support for HPW
- The primary structure of polyanion remained intact on the carbon support
- Strong interaction between the carbon support and heteropoly anion through the corner shared oxygen (W-$O_c$-V) of the polyanion is observed
- The catalytic performance of HPW/Carbon catalysts for the synthesis of MTBE is comparable to that of mesoporous silica based catalyst

# V. Adsorptive Desulphurization Process - Application of Carbon Materials

## Objectives:

- Develop suitable adsorbents for desulfurisation
- Adsorbent - Reduction of S from 700 ppm to > 300 ppm
  Regenerable to sustain continuous operation
  Work under mild operating conditions

- A simple, inexpensive and efficient process for desulphurisation is designed

## Sulphur Adsorption Process

Adsorbent (5, 10, 15, 100 g)

↓

Packed in a glass column held in vertical position

↓

CBR diesel fed through a burette held vertically above the column

↓

Feed passes through carbon bed slowly

↓

Product collected at the bottom of the column (out let) in 20 ml aliquots

↓

S content in the product analyzed by XRF and S components by GC-PFPD

“Adsorptive desulphurization carried out in a simple experimental set up at RT and atmospheric pressure”

# S sorbing ability of different commercial activated carbon materials

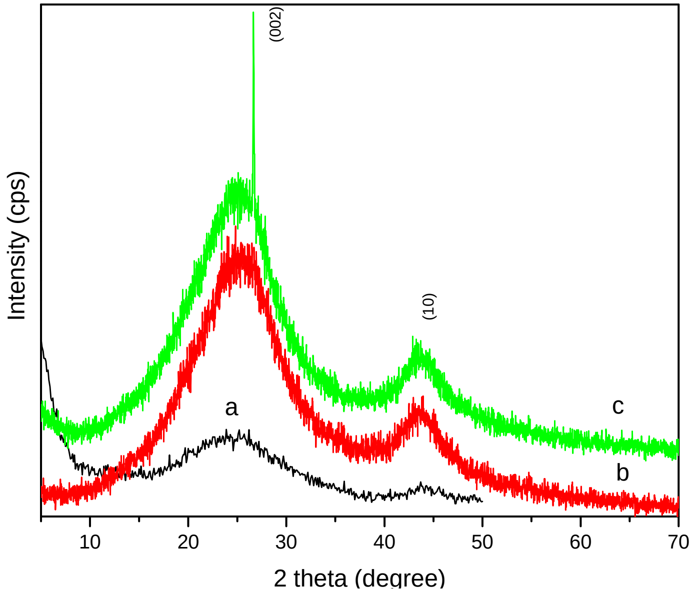
| S. No. | Activated Carbon as Sorbent | *ml-diesel treated/ g of adsorbent | S removed (ppm) |
|---|---|---|---|
| 1 | IG 18 x 40 | 4 | 134 |
| 2 | IG 12 x 10 | 4 | 81 |
| 3 | IG 8 x30 | 4 | 76 |
| 4 | AC 4 x 8 | 4 | 12 |
| 5 | AC 6 x 12 | 4 | 73 |
| 6 | AC 12 x 30 | 4 | 92 |
| 7 | Calgon carbon as received | 4 | 181 |
| 8 | Adsorbent carbon | 4 | 229 |

***20 ml initial product collected from the column packed with 5.0 g activated carbon and analyzed for S**

- ➢ Adsorbent carbon as received and Calgon carbon as received showed outstanding performance by adsorbing 229 and 181 ppm of S per g of adsorbent from 4 ml of treated diesel

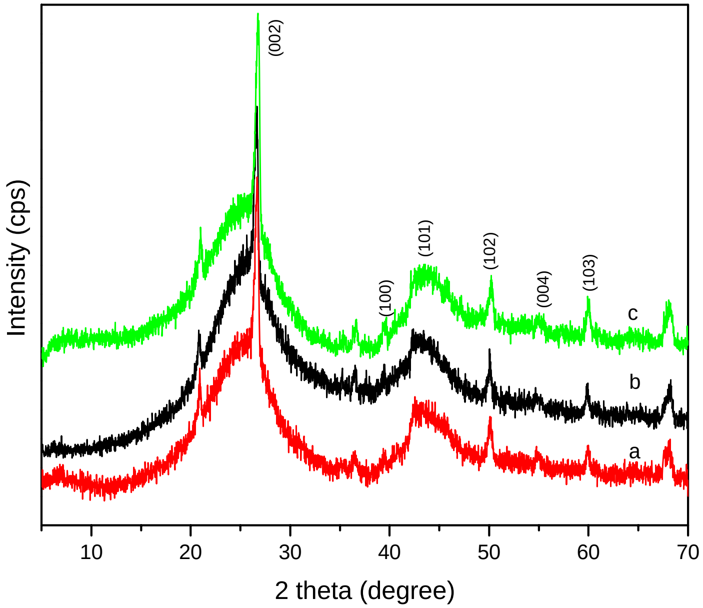
- ➢ So intensive studies of adsorptive desulphurisation were carried out on Adsorbent carbon and Calgon carbon

# Modified Adsorbent (AC) and Calgon Carbon (CC) – Structural and Textural Properties



(a) AC as received, b) AC treated with $HNO_3$
(c) AC treated with $HNO_3$ and activated with Ar

- Crystallinity of nitric acid treated adsorbent carbon increased upon Ar activation at 800 ° C

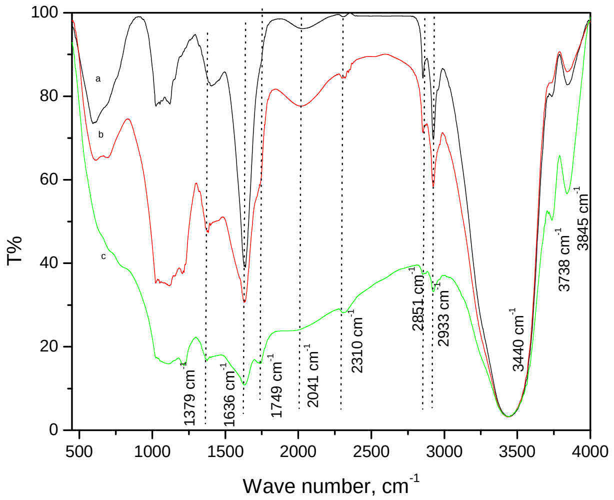


(a) CC as received, (b) CC treated with $HNO_3$ and
(c) CC treated with $HNO_3$ followed by Ar activation

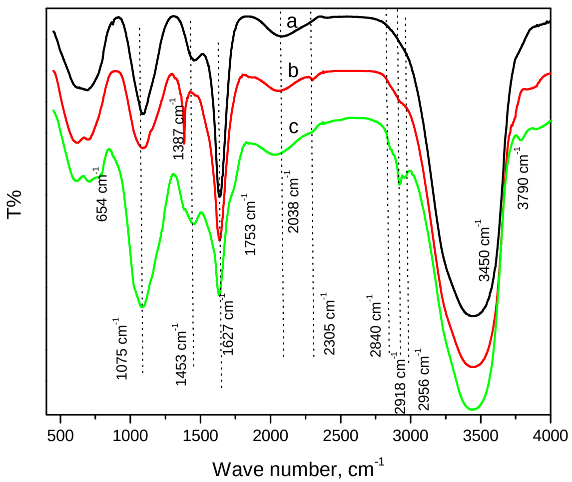
- Diffraction peaks are typical of graphitic carbon structure
- Calgon based carbons are structurally more ordered than adsorbent based carbons

| Sample | Carbon Sorbent | $S_{BET}$ ($m^2/g$) | Vp ($cm^3/g$) |
|---|---|---|---|
| a | Adsorbent Carbon as received | 950 | 0.451 |
| b | Adsorbent Carbon treated with conc. $HNO_3$ | 882 | 0.398 |
| c | Adsorbent Carbon treated with conc. $HNO_3$followed by Ar activation | 1048 | 0.523 |
| d | Calgon carbon as received | 1014 | 0.587 |
| e | Calgon carbon treated with conc. $HNO_3$ | 649 | 0.387 |
| f | Calgon carbon treated with conc. $HNO_3$ followed by ar activation | 996 | 0.598 |

# Modified Adsorbent (AC) and Calgon Carbon (CC) – Surface Functionality



FT-IR spectra of (a) Adsorbent carbon as received, (b) Adsorbent carbon treated with $HNO_3$ (c) Adsorbent carbon treated with $HNO_3$ and activated with Ar



FT – IR spectra of (a) calgon carbon as received, (b) calgon carbon treated with $HNO_3$ and (c) calgon carbon treated with $HNO_3$ followed by Ar activation

## S sorption capacity – Adsorbent Carbon Vs Calgon Carbon

| Sorbent Amount | 5.0 g | 10.0 g | 15.0 g |
|---|---|---|---|
| Sorbent Type | S removed*, (in ppm) | | |
| Adsorbent carbon as received | 229 | 380 | 410 |
| Adsorbent carbon treated with $HNO_3$ | 105 | 186 | 577 |
| Adsorbent carbon treated with $HNO_3$ followed by Ar activation | 346 | 518 | 586 |
| Calgon carbon as received | 181 | 371 | 451 |
| Calgon carbon treated with $HNO_3$ | 280 | 378 | 488 |
| Calgon carbon treated with $HNO_3$ followed by Ar activation | 340 | 399 | 619 |

# Adsorptive Desulphurization – Removal of refractory S compounds

| Sulphur Species | S content (in ppm) | | |
|---|---|---|---|
| | CBR diesel (Feed) | Adsorbent carbon $HNO_3$ followed by Ar treatment, 15.0 g | Calgon carbon, $HNO_3$ followed by Ar treatment, 15.0 g |
| $C_1BT$ | 4.6 | Nil | Nil |
| $C_2BT$ | 119.6 | Nil | Nil |
| $C_3BT$ | 137.5 | 75.2 | 67.2 |
| $C_3^+BT$ | 79.6 | 68.9 | 47.4 |
| DBT | 91.5 | 2.6 | 1.3 |
| $C_1DBT$ | 157.7 | Nil | Nil |
| $C_2DBT$ | 116.7 | Nil | Nil |
| $C_3DBT$ | 29.5 | 4.3 | 2.1 |
| Total S | 737 | 151 | 118 |

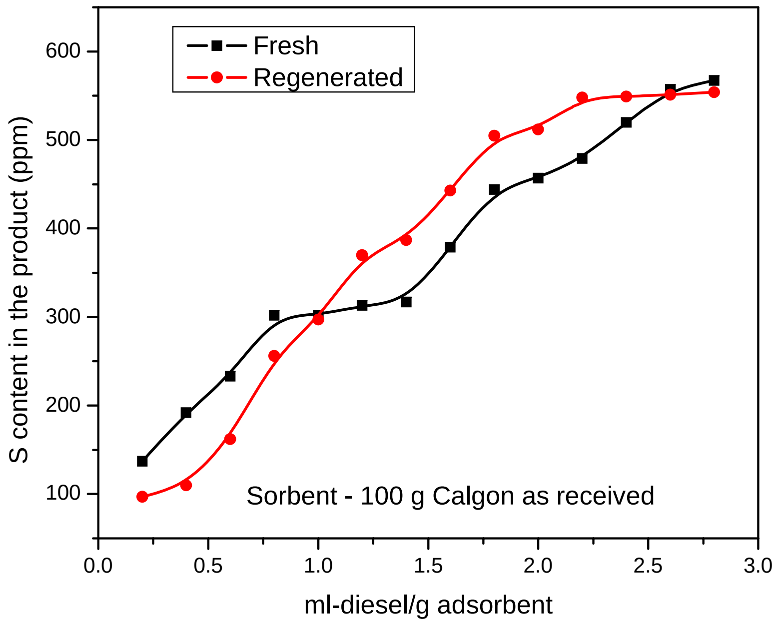
Analyzed by GC – PFPD

- Adsorptive desulphurization process removed refractory S compounds more easily compared to conventional hydrodesulphurization process

V. Selvavathi, A. Meenakshisundaram, B. Sairam, P. Indra Neel, M. Rajasekaren, B. Viswanathan
6th International symposium on Fuels and Lubricants (ISFL – 2008), March 9 – 12, 2008 at New Delhi

# Process Scaling up & Adsorbent Regeneration Methods

| **S. No.** | **ml-diesel/g adsorbent** | **S content in the product (S content removed) (in ppm)** | |
|---|---|---|---|
| | | Adsorbent carbon activated with $HNO_3$ followed by Ar activation | Calgon carbon as received |
| 1 | 0.2 | 13 (724) | 137 (600) |
| 2 | 0.4 | 68 (669) | 192 (545) |
| 3 | 0.6 | 110 (627) | 233 (504) |
| 4 | 0.8 | 169 (568) | 302 (435) |
| 5 | 1.0 | 194 (543) | 302 (435) |
| 6 | 1.2 | 233 (504) | 313 (424) |
| 7 | 1.4 | 263 (474) | 317 (420) |
| 8 | 1.6 | 290 (447) | 379 (358) |
| 9 | 1.8 | 325 (412) | 444 (293) |
| 10 | 2.0 | 375 (362) | 457 (280) |
| 11 | 2.2 | 415 (322) | 479 (258) |
| 12 | 2.4 | 443 (294) | 520 (217) |
| 13 | 2.6 | 463 (274) | 557 (180) |
| 14 | 2.8 | 486 (251) | 567 (170) |
| 15 | 3.0 | 496 (241) | 519 (218) |
| 16 | 3.2 | 505 (232) | 532 (205) |
| 17 | 3.4 | 510 (227) | 548 (189) |



**S removal capacity of fresh vs toluene regenerated sorbent**

## Summary:

- An efficient desulphurization process based on adsorption, operated under modest conditions of temperature and pressure is developed

- The potential of the process of adsorptive desulphurization lies in the elimination of refractive S containing compounds under mild process parameters

- New method of activation, which is a unique combination of nitric acid treatment and Ar activation, of carbon based adsorbents to induced desired surface functionality, polarity, phase composition and pore texture, is developed

- It was found that subsequent Ar activation of nitric acid treated carbon adsorbents are inevitable to derive the best out of oxidative modification of carbon surface chemistry

- The utility of Adsorbent carbon as well as Calgon carbon and their tailored forms as adsorbents for organo sulphur compounds is elucidated

- The process of adsorptive desulphurization is scaled upto 100 g (adsorbent) batch

- A simple, inexpensive, efficient, environmentally benign and reliable solvent (toluene) based regeneration has also been developed.

# Conclusion

**Patent:**

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2. R. Mahalaxmi, P. Indra Neel and B. Viswanathan, Functionality of Carbon Surfaces, Indian Journal of Chemistry Section A, (Accepted)

**National/International conferences:**

1. P. Indra Neel, B. Viswanathan, T. K. Varadarajan, Preparation, Characterization and Evaluation of Catalytic Activity of dodeca tungsto phosphoric acid (HPW) and dodeca tungstosilicic acid (HSiW) supported on SBA-I mesoporous silica" 17th National symposium on Catalysis, 18-20th January, 2005, CSMCRI, Bhavnagar, Gujarat, India
2. P. Indra Neel, B. Viswanathan, T. K. Varadarajan, Spectroscopic analysis of supported heteropoly acid catalysts, International Conference on Spectrophysics, INCONS-2005, 9-12th , February, 2005, Pachaiyappa's college, Chennai, India
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